BASE CLEAVAGE OF THE ARYL-SILICON BOND

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1973

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ABSTRACT

The rate constants for the cleavage of the series of substituted phenyltrimethylsilanes by KOH in aqueous DMSO have been measured, and the pattern of substituent effects is shown to be consistent with a mechanism involving rate determining separation of a phenyl carbanion accompanied by electrophilic assistance from the solvent. A number of heterocyclic trimethylsilyl derivatives have also been cleaved and the rates are discussed in terms of the proposed mechanism.

Cleavage also occurs using other highly basic nucleophiles, and there is excellent correlation between the rate constants for cleavage and the acidity functions of the media used. Although all dipolar aprotic solvents greatly enhance the nucleophilicity of small anions because of the absence of solvation, DMSO has the apparently unique ability to facilitate cleavage in the reaction which was studied.

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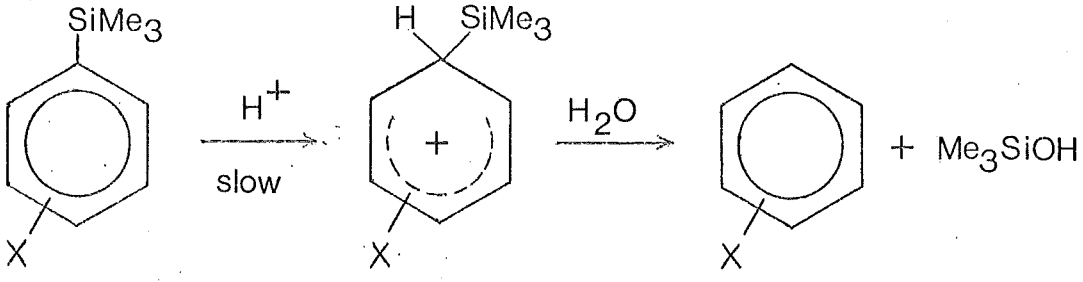
INTRODUCTION

Silicon is more electropositive than carbon; on Pauling's scale, the electronegativity difference is 0.7 units[1]. Hence the C-Si bond is more polar than, for example, the C-Cl bond. Since the bond is polarized $C^{\delta-}$ — $Si^{\delta+}$, electrophilic attack occurs at carbon, and nucleophilic attack at silicon. The C - Si bond is relatively strong, (ionic bond strength 932 kJ/mole[1]) so that cleavage only occurs readily if suitable polar groups are present to stabilize the transition state. Hence, in the aryltrialkylsilanes, the subject of this investigation, the aryl-silicon bond, rather than the alkyl-silicon bond, is the most susceptible to cleavage.

ELECTROPHILIC CLEAVAGE OF THE ARYL-SILICON BOND

Electrophilic cleavage of the phenyl-silicon bond in such media as $H_2SO_4/HOAc/H_2O$ [2], $HClO_4/MeOH$ [3] and $Br_2/HOAc$ [4] has been extensively studied. In all cases, the pattern of substituent effects is similar to that established for electrophilic aromatic substitution, with excellent correlation of relative rates with the σ^+ substituent constants proposed by Brown and Okamoto[5].



Hence reaction is facilitated by conjugative electron release if the transition state is assumed to be structurally similar to the intermediate[6]. Formation of the intermediate appears to be rate determining, as the sensitivity of reaction rates to H - D exchange ($\frac{K_{H_2O}}{K_{D_2O}} \sim 1.55$) indicates that C - H bond formation has advanced significantly in the rate determining step[7].

NUCLEOPHILIC CLEAVAGE OF THE ARYL-SILICON BOND

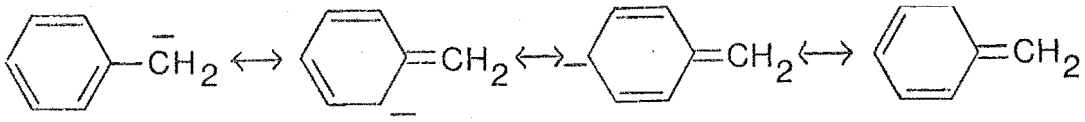
Nucleophilic cleavage of the phenyl-silicon bond has proved much more difficult to achieve than electrophilic cleavage. Perhaps the best explanation is that, in contrast to electrophilic cleavage, no resonance stabilization is possible in the transition state, since any negative charge developed on the aryl carbon cannot be delocalized through the π system. Although the bond can be cleaved in a medium such as KNH_2/NH_3 [8], cleavage by alkali, until now, has only been reported at high temperature (100°C) and with strongly electron-withdrawing substituents, such as $\underline{p}$-NO_2 and $\underline{m}$-CF_3, on the benzene ring[9,10]. In contrast, aromatic centres which can stabilize negative charge either inductively or by resonance stabilization, are quite readily cleaved from silicon. Aromatic derivatives containing electronegative hetero atoms such as sulphur, oxygen and nitrogen, cleave readily. 2-Trimethylsilylfuran is cleaved in alkali[11], and 2-trimethylsilylpyridine is cleaved even by neutral polar reagents such as methanol[12] and benzaldehyde[13]. In the series $R\text{-}SiPh_3$, reaction with alkali follows the same order as the acidity of the corresponding hydrocarbons R - H, acidity being a measure

of carbanion stability[9].

R = $PhC \equiv C-$ > 1-indenyl, 9-fluorenyl > Ph_2CH- > $PhCH_2-$

> m-$CF_3C_6H_4-$ > p-ClC_6H_4- >> Ph -

Consequently, base cleavage in series such as $XC_6H_4CH_2SiMe_3$ [14] and $XC_6H_4C \equiv CSiMe_3$ [15] has been extensively studied, since reaction is facilitated by π-delocalization of carbanion character developed in the transition state.

e.g. 

Until the work reported in this thesis, no systematic study of phenyl-silicon cleavage by nucleophiles had been carried out. For reasons explained later, use of a dipolar aprotic solvent such as dimethylsulphoxide facilitates reaction, making this investigation possible.

NUCLEOPHILICITY AND BASICITY IN PROTIC AND DIPOLAR APROTIC SOLVENTS

The generally held concept is that both bases and nucleophiles are species which have a tendency to share their electron pairs. The term basicity is generally used in a thermodynamic sense for affinity towards a proton:

$$B^- + H_2O \rightleftharpoons BH + OH^-$$

The acid dissociation constant K_a of the conjugate acid BH is a measure of the basicity of B^-.

Nucleophilicity is used in a kinetic sense to denote the ability to displace another electron pair from a species:

$$N^- + R-Y \xrightarrow{k} N-R + Y^-$$

The rate constant k is a measure of the nucleophilicity of N^-.

Where a series of nucleophiles are structurally related, there is usually correlation between their nucleophilicity and basicity; however, only in this limited context can one assume a direct relationship. The structural and electronic features which enhance nucleophilic reactivity in displacement reactions do not necessarily play a significant role in acid-base equilibria[16].

Since basicity is an inadequate basis for predicting nucleophilic activity, considerable effort has been made to set up a scale of nucleophilicity which can be generally applied. Swain and Scott[17] suggested a scale for use in S_N2 displacement reactions based on the solvolysis of methyl bromide as a standard reaction.

$$\log \frac{k_{N^-}}{k_{H_2O}} = s.n \qquad (1)$$

k_{N^-}, k_{H_2O} are second order rate constants for displacement by nucleophile and water respectively, s is the substrate constant (1.00 for CH_3Br), and n is the nucleophilic constant (1.00 for H_2O). Typical values for these parameters are shown in Table 1.

Table 1

n Values for Typical Nucleophiles[17]

Nucleophile	n	Nucleophile	n
$S_2O_3^{2-}$	6.36	Br^-	3.89
SO_3^{2-}, CN^-	5.1	Cl^-	3.04
I^-	5.04	AcO^-	2.72
SCN^-	4.77	F^-	2.0
$PhNH_2$	4.49	picrate	1.9
OH^-	4.20	NO_3^-	1.03
N_3^-	4.00	H_2O	1.00

However, the range of data which can be correlated is generally limited to that for reactions involving attack at saturated (sp^3) carbon. A less empirical approach, suggested by Edwards[18] and refined by Edwards and Pearson[19,20] is based on the assumption that the nucleophilicity of a species is governed by both its basicity and polarizability. The dependence on basicity is justified on the grounds that most nucleophilic reactions are either acid-base reactions, or involve attack on a species which bears some resemblance to a proton, either in size or charge. If a species is polarizable it should be more nucleophilic, as, not only will bonding electrons tend to orient themselves towards a substrate, but non-bonding electrons will be able to orient themselves away from it. Hence closer approach is made possible by reducing repulsions between nucleophile and substrate. The Edwards and Pearson expression is

$$\log k_{rel} = AP + BH \quad (2)$$

where k_{rel} is the rate constant for a nucleophile relative to water, P is a polarizability term based on the molar refractivity of the nucleophile relative to water, and H is a basicity term relative to water.

$$H = 1.74 + pK_a \quad (3)$$

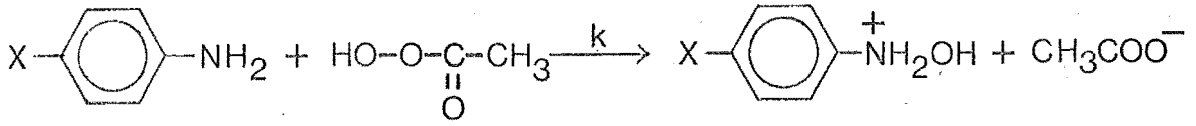
where pK_a is the dissociation constant of the conjugate acid of the nucleophile - 1.74 arises from the pK_a of H_3O^+. The values of the coefficients A and B supposedly reflect the contributions of the two factors to the overall nucleophilicity of the species in a particular reaction; however quantitatively, correlations are poor. Values of P and H for common nucleophiles are shown in Table 2.

Table 2

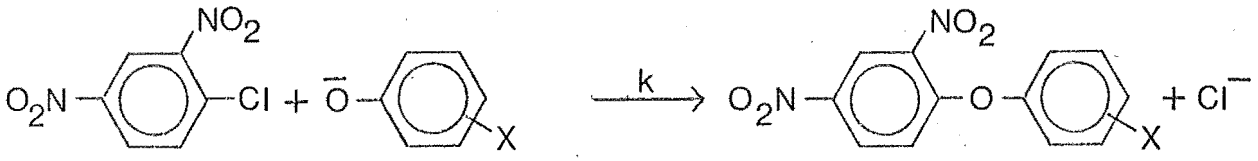
P and H Values for Typical Nucleophiles

Nucleophile	P	H	Nucleophile	P	H
CN^-	0.373	10.88	Br^-	0.539	≈-6.0
I^-	0.718	-9.00	Cl^-	0.389	≈-3.0
$PhNH_2$	0.955	6.3	AcO^-	-	6.46
$PhNMe_2$	1.046	6.95	F^-	-0.150	4.9
NEt_3	0.955	12.46	NO_3^-	0.00	0.40
NH_3	0.184	11.22	H_2O	0.00	0.00
OH^-	0.143	17.48			
N_3^-	0.524	6.46			

For acid-base reactions, and for nucleophilic attack at carbonyl carbon, tetrahedral sulphur, and tetrahedral phosphorus, basicity is the most important factor, while for attack at tetrahedral carbon, divalent oxygen, and halogens, polarizability is more important[20]. Within a series of structurally related nucleophiles, polarizability should be relatively constant, so that correlation between nucleophilicity and basicity should occur. For example, in the nucleophilic attack of <u>para</u> substituted anilines on peracetic acid there is good correlation between the rate constants and the basicities of the anilines[21].



Similarly, for nucleophilic attack by substituted phenoxides on 2,4-dinitrochlorobenzene, the rate constants correlate with basicities of the phenoxides. The results for methoxide ion do not fit in with the correlation[22].



SOLVENT EFFECTS ON NUCLEOPHILICITY AND BASICITY

An additional factor which must be considered in discussing nucleophilicity is the effect of solvent. The attempts outlined so far to quantitatively define nucleophilicity have been carried out in protic solvents such as water and methanol. Protic solvents solvate ions not only by ion-dipole interaction, but, more importantly, by strong hydrogen bonding. Hydrogen bonding is greatest for small, densely charged, anions of low polarizability so that for a range of typical nucleophiles the order of solvation is

$$OH^-, F^- >> Cl^- > Br^- > N_3^- > I^- > SCN^- > \text{picrate}.$$

Because of hydrogen bonding, the basicity of anions such as OH^- and F^- is severely reduced, and nucleophilicity in protic solvents is largely a function of polarizability. For example, nucleophilicity towards methyl iodide in methanol follows the order

$$S_2O_3^{2-} > I^- > SCN^- \approx CN^- > N_3^- \approx Br^- > Cl^- > AcO^- > F^-, OH^-;$$

as illustrated by the data in Table 3.

Dipolar aprotic solvents such as DMSO, acetone and DMF, cannot solvate anions by hydrogen bonding and may also be hindered in participating in other ion-dipole interactions. In DMSO, for example, it is thought that ion-dipole solvation via the electropositive sulphur atom may be sterically inhibited by the surrounding methyl groups[24]. Solvation occurs largely by interactions dependent on polarizability, so that the order of anion solvation is probably the reverse of that in protic solvents, i.e.

$$\text{picrate} > SCN^- > I^- > N_3^- > Br^- > Cl^- >> F^-, OH^-.$$

Table 3

Second Order Rate Constants for Nucleophilic Attack on Methyl Iodide in Methanol at 25°C [23]

Nucleophile	$10^3 k_2$ ($\ell.mol^{-1}sec^{-1}$)	Nucleophile	$10^3 k_2$ ($\ell.mol^{-1}sec^{-1}$)
PhS^-	1070	N_3^-	0.078
$S_2O_3^{2-}$	114	PhO^-	0.073
I^-	3.42	$PhNH_2$	0.052
CN^-	0.645	NH_3	0.041
NEt_3	0.595	C_5H_5N	0.022
SCN^-	0.574	Cl^-	0.003
MeO^-	0.251	AcO^-	0.0027
Br^-	0.0798	F^-	0.00005

Nucleophilicity in dipolar aprotic solvents should therefore be largely dependent on basicity; because of the absence of hydrogen bonding, small highly basic anions such as OH^-, F^-, CN^- should be the best nucleophiles. For attack on methyl iodide in DMF[23], nucleophilicity follows the order $CN^- > AcO^- > Cl^- \approx Br^- \approx N_3^- > I^- > SCN^-$. A similar order (Table 4) is reported for the nucleophilic substitution of n-propyl tosylate in DMSO[25].

Overall nucleophilicity is further enhanced because transition states in most nucleophilic substitution reactions are usually large diffuse anions, and are more effectively solvated by dipolar aprotic solvents than by protic solvents. The resulting decrease in activation energy markedly increases reaction rates.

Table 4

Rate Constants for Substitution in n-Propyl Tosylate[25]

(DMSO, 25°C)

Nucleophile	$10^5 k_2$ ($\ell.mol^{-1}sec^{-1}$)
$S_2O_3^{2-}$	9.4×10^4
OH^-	2.9×10^4
MeO^-	2.7×10^4
F^-	2.0×10^4
PhO^-	2.6×10^3
N_3^-	270
Cl^-	95
Br^-	41
SCN^-	3.4

Even thiocyanate ion, which should be a better nucleophile in protic solvents, attacks methyl iodide one hundred times faster in DMF than in methanol, while fluoride ion attacks one million times faster[23].

PROTIC-DIPOLAR APROTIC SOLVENT MIXTURES

Many anionic nucleophiles are so poorly solvated in dipolar aprotic solvents that they are insoluble. They are, however, moderately soluble in mixtures of dipolar aprotic and protic solvents. For example, species such as KOH, KCN and NaOAc are moderately soluble in DMSO/water and DMSO/methanol mixtures. The enhanced nucleophilic activity of anions is retained, even when the mole percentage of protic solvent is

high. The most reasonable explanation for this behaviour is that solvents such as DMSO, being relatively strong bases, can hydrogen bond to protic solvent molecules, which are then no longer free to solvate anions. There is, for example, some evidence that DMSO forms a 1:2 adduct with water. The viscosity of H_2O/DMSO reaches a maximum when the mole percentage of DMSO is 33%, suggesting a high degree of order. The molar heat of mixing reaches a maximum when the mole percentage of DMSO is between 30% and 40%, and the freezing point composition curve shows an eutectic when the mole percentage of DMSO is 33%[26]. Further evidence is the recent isolation of a crystalline 1:2 adduct between DMSO and 2,5-t-butylmethylphenol[27]. Hence in a medium such as H_2O/DMSO, anions would have to compete with DMSO for hydrogen bonding with water.

PARTICIPATION OF d-ORBITALS IN BONDING AT SILICON

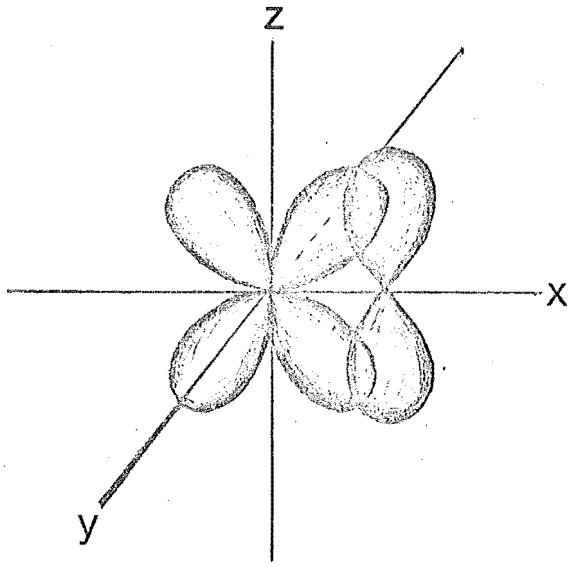
Before discussing possible mechanisms for substitution, the type of bonding associated with silicon must be considered.

Both carbon and silicon are Group IV elements, so that both elements adopt sp^3 hybridization to form tetravalent compounds. Silicon however, being a second row element, possesses vacant d orbitals energetically accessible for bonding, and there is evidence that the use of d-orbitals in bonding may lead to (i) partial π-bonding, and (ii) the formation of penta- or hexacovalent complexes and intermediates.

(i) Partial π-bonding

No compounds with multiple (p-p)π bonds to silicon have so far been isolated, although they may exist as unstable

intermediates[28]. Although this lack of multiple bonding is a common feature of second row elements, the reason for it is not clear. One suggestion is that compared with first row elements, there is greater interatomic repulsion between the inner filled shells and the bonding orbitals of the adjacent atom, resulting in less effective p-p orbital overlap[29]. Alternatively, it may be that since internuclear distances are much greater in second row elements, p-p orbital overlap is insufficient for bonding[29,30]. Calculations indicate that (p-p)π interaction in the silicon-silicon bond is about half that in the carbon-carbon bond[31]. In contrast to the absence of (p-p)π bonding, it has been shown from overlap integral calculations that the vacant d_{xy}, d_{xz} and d_{yz} orbitals of silicon and other second row elements can overlap effectively with appropriately oriented p orbitals of an adjacent atom, to give (d-p)π bonding[32].



$(d_{xz}$-p)π overlap

There is considerable evidence in favour of such partial (d-p)π bonding, particularly in cases where the adjacent atom possesses non-bonding outer electrons. Trisilylamine, $N(SiH_3)_3$, is a considerably weaker base than trimethylamine;

from a comparison of the electronegativities of silicon and carbon, one would expect it to be a stronger base. This indicates a significant contribution of structures such as $H_3\overset{-}{S}i=\overset{+}{N}(SiH_3)_2$, especially since the molecule appears to be planar[33]. Other anomalies which have a similar explanation include the high acidity of trimethylsilanol relative to t-butyl alcohol[34], and the apparent linear structure of hexamethyldisiloxane[35]. An n.m.r. study of the series Me_3SiX showed moderately strong (d-p)π bonding for $X = NMe_2$, OMe and F [36].

There is also evidence of (d-p)π bonding in the carbon-silicon bond, and, more specifically, the aryl-silicon bond[28]. Dipole moment studies in the series $p\text{-}XC_6H_4SiMe_3$ show partial (d-p)π bonding between silicon and the ring, even when X is not a conjugatively electron-releasing group[37,38]. Structures such as (a) and (b) in Fig. 1 therefore make a significant contribution to the ground state of their respective molecules.

(a) (b)

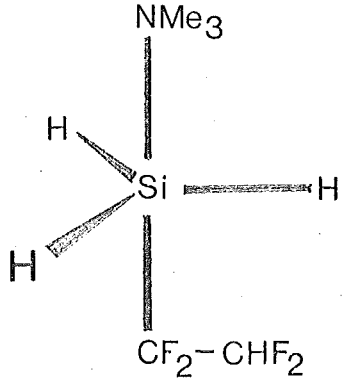
Fig. 1

Similar results were obtained in the trimethylphenyltin series[39]. Analysis of e.s.r. spectra of the radical ions from tert-butylbenzene, phenyltrimethylsilane and phenyltrimethylgermane shows that silicon, and to a lesser extent, germanium, strongly attract π electrons[40]. Calculations based

on e.s.r. studies of trimethylsilyl derivatives of biphenyl indicate a π-bond order of 0.18[41]. There is good agreement between the u.v. spectral intensities of substituted phenylsilanes, and the intensities calculated on the assumption of d-orbital participation[42]. As other investigations have shown, d-orbital participation decreases in the Group IVb metals, Si > Ge > Sn.

(ii) Formation of complexes and intermediates

As well as (d-p)π bonding, there is evidence of d-orbital participation in σ bonding, with sp^3d or sp^3d^2 hybridization giving rise to penta- or hexacovalent complexes or intermediates. The most common examples of hexacovalency are the hexafluorosilicate ion SiF_6^{2-}, shown to be octahedral by X-ray studies[43], and the tris(acetylacetonato) silicon IV complex, ($A_3Si^+.HCl_2^-$, A = acetylacetonato) also shown to be octahedral[44]. Other examples are mostly complexes formed from silicon halides and amines, such as $SiF_4.2NMe_3$, $SiCl_4.2C_5H_5N$, and $SiF_4.2C_5H_5N$[1]. There is less evidence of pentacovalency. Although complexes such as $SiCl_4.NMe_3$, $H_3SiCl.NMe_3$, $SiF_4.NMe_3$ etc. are known, there is some doubt whether these are pentacovalent complexes, since $H_3SiI.NMe_3$ is known to be a salt $H_3\overset{+}{S}iNMe_3I^-$ [1]. More promising evidence is the recent isolation of a complex $CHF_2 - CF_2 - SiH_3.NMe_3$; shown, by n.m.r., to have equivalent hydrogens, which suggests a bipyramidal complex[45].



Most known complexes contain strongly electronegative atoms, such as oxygen, fluorine and chlorine. This is consistent with a recent suggestion that, since the bonds to such atoms have considerable ionic character, the electron density on the central atom is reduced. This should promote contraction of d-orbitals to a size more suited to effective hybridization with s and p orbitals; as a result, complexes may form since additional σ bonds are possible[46].

However, studies based on replacing the acetylacetonato groups by alkyl groups in A_3Si^+ compounds (A = acetylacetonato) indicate that the presence of alkyl groups at silicon reduces the possibility of complex formation[47,48].

POSSIBLE MECHANISMS FOR NUCLEOPHILIC SUBSTITUTION

In substitution at sp^3 carbon, there is often no clear distinction between the S_N1 and S_N2 mechanisms; in substitution at silicon the distinction is even less clear, as the difference between a synchronous mechanism and one involving intermediate formation may only be a matter of degree. For the purpose of this discussion, however, the mechanisms for nucleophilic substitution at silicon and other Group IVb metals fall into two categories:

(i) S_N2 (analogous to S_N2 substitution at sp^3 carbon)

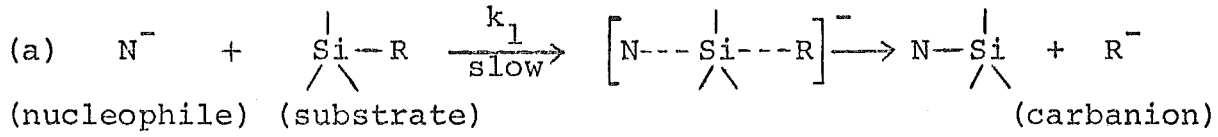
(ii) via an intermediate.

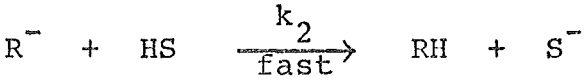
In addition, carbanion formation may or may not occur.

The possible mechanisms and their probable kinetics are outlined, and the current evidence pertaining to substitution discussed. Rate equations were derived by using the Steady State theory.

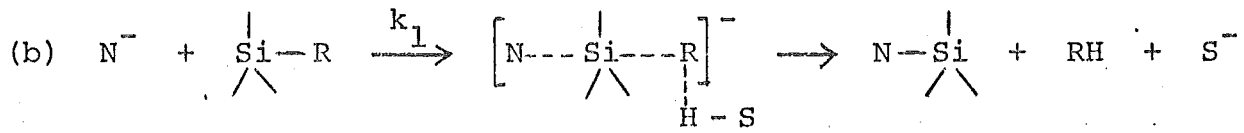
(i) S_N2

Reaction follows a path similar to S_N2 substitution at sp^3 carbon; bond making and breaking are more or less synchronous, although bond making could precede bond breaking to give some small build-up of negative charge on the central atom. Either (a) a carbanion is generated which extracts a proton from the solvent in a subsequent fast step, or (b) solvent is involved in the rate determining step so that a formal carbanion does not develop.





rate = $k_1[N^-][\equiv Si\text{-}R]$



rate = $k_1[N^-][\equiv Si - R][HS]$

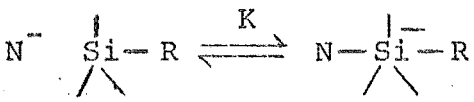
The reaction should be stereospecific with inversion, since backside attack should be favoured for two reasons; (i) sterically, if the nucleophile or leaving group is bulky, and (ii) because nucleophile and leaving group should be collinear if both are to share the same hybridized orbital of silicon. In the transition state, the other three orbitals should approach coplanarity, especially if the nucleophile and leaving group are similar.

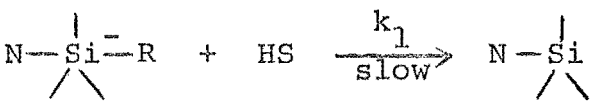
(ii) Via an Intermediate

Silicon could utilize a vacant 3d orbital, to enable formation of a pentacovalent intermediate with sp^3d configuration. $sp^3d_{z^2}$ hybridization to give a trigonal bipyramidal intermediate is considered to be only slightly more probable than $sp^3d_{x^2-y^2}$ hybridization to give a square pyramidal intermediate[49]. Unless necessitated by steric factors, intermediate formation would not require rear attack (i.e. on the opposite side to the leaving group) by a nucleophile, although it is believed that electronegative groups prefer to overlap with hybrid orbitals containing the least possible s character which in the trigonal bipyramid case, would be the axial (pd) orbitals[50]. The possible mechanisms split into two groups, depending on whether a carbanion is formed.

(a) No carbanion formation

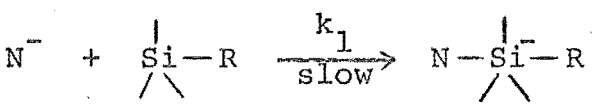
(i) rapid equilibrium intermediate formation followed by slow reaction with solvent

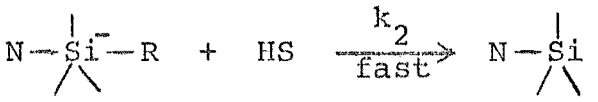




$$\text{rate} = k_1K[N^-][\equiv Si-R][HS]$$

(ii) slow intermediate formation followed by rapid reaction with solvent

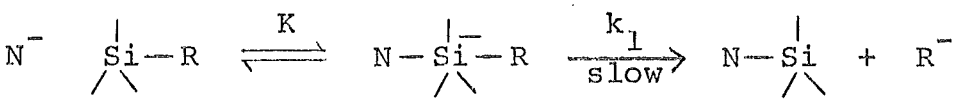


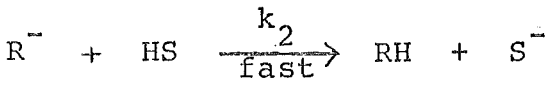


$$\text{rate} = k_1[N^-][\equiv Si-R]$$

(b) Carbanion formation

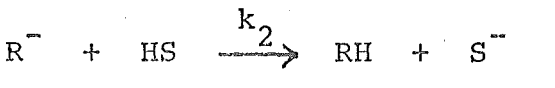
(i) rapid equilibrium intermediate formation, followed by slow formation of carbanion





rate = $k_1K[N^-][\equiv Si - R]$

(ii) slow intermediate formation followed by equilibrium formation of carbanion



rate = $k_1[N^-][\equiv Si - R]$

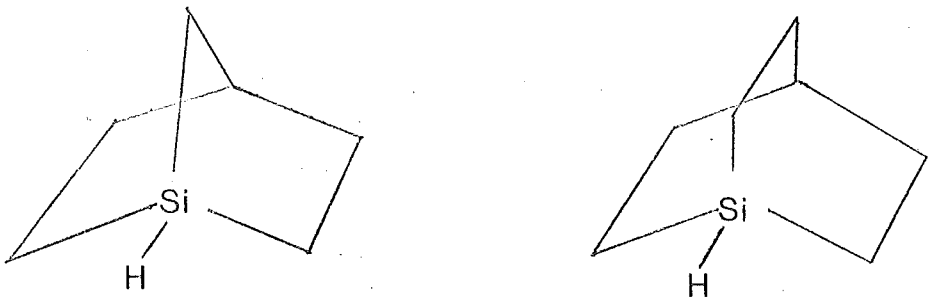
MECHANISTIC EVIDENCE

Unfortunately, kinetic studies are insufficient to distinguish between possible mechanisms, as all are first order in both nucleophile and substrate. For example, alkali cleavage of substituted benzyltrimethylsilanes[14], phenoxytriethylsilanes[51] and methylfurylsilanes[52] all display overall second order kinetics consistent with any of the suggested mechanisms. Most of the useful evidence comes from studies involving stereochemistry, isotope effects, and substituent effects.

(i) S_N2 versus intermediate formation

Hammett relationships derived from alkali cleavage in series such as the substituted benzyltrimethylsilanes[14], (phenylethynyl)trimethylsilanes[15], and phenoxyltriethylsilanes[51] all exhibit positive ρ values, as electron-withdrawing substituents enhance and electron-releasing substituents retard reaction. This is consistent with both the S_N2 and intermediate pathways as it merely indicates development of negative charge in the transition state at the reaction site, which could be either silicon or the leaving group. However, benzyltriphenylsilane cleaves more rapidly in alkali than benzyltri(p-tolyl)silane[14], and as the methyl group is electron-releasing, this indicates an increase in the negative charge on silicon in the transition state of the rate determining step. Although this rules out a synchronous S_N2 mechanism, it does not exclude an S_N2 mechanism in which bond formation slightly precedes bond breaking to give some negative charge build up on silicon.

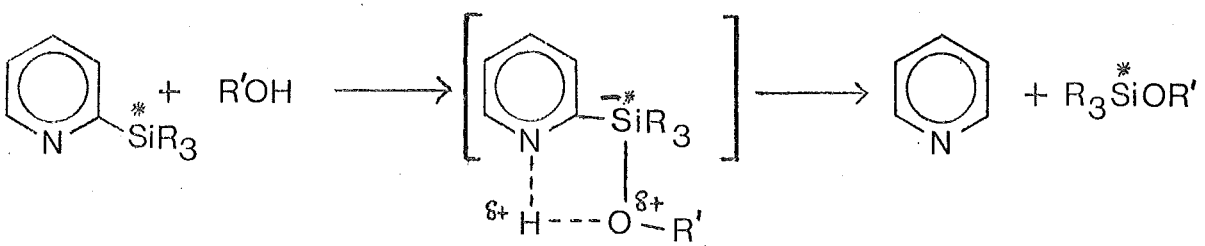
Stereochemical evidence favours intermediate formation accompanied by assistance from the electrophilic portion of the nucleophile or solvent. As previously mentioned, rear attack relative to the leaving group is a prerequisite for S_N2 substitution, and results in inversion of configuration. However, intermediate formation could arise from either rear or flank attack and ultimately result in either inversion or retention respectively. There is clear evidence that substitution can involve flank attack. Substitution by alcoholic alkali at the bridgehead silicon atom in compounds (a) and (b) in Fig. 2 occurs at least as readily as in structurally similar compounds such as triethylsilane[53,54].



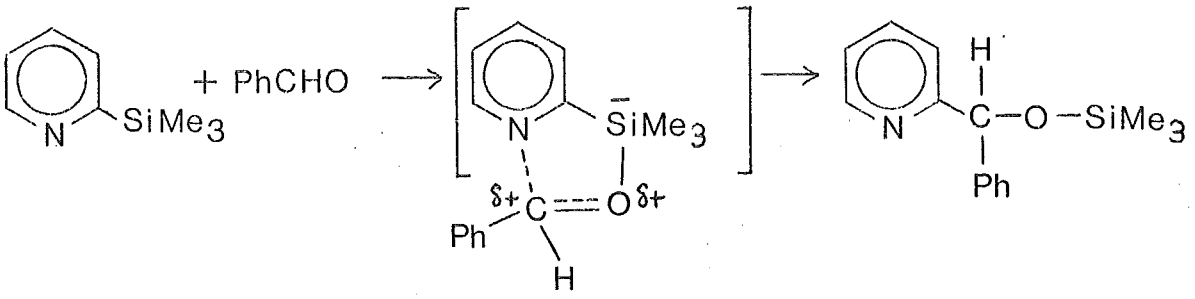
(a) (b)

Fig. 2

Since nucleophiles are unable to approach silicon from the rear because of steric hindrance, flank attack must be involved. Even in cases where both rear and flank attack should be possible, flank attack appears to predominate, probably because the electrophilic portion of the reagent is then sufficiently close to assist the leaving group. For example, complete retention of configuration may occur in the alcoholysis of (+) 2-(methyl 1-napthylphenylsilyl) pyridine because flank attack facilitates formation of a cyclic intermediate involving the adjacent nitrogen[55].



A similar mechanism would explain the product in the reaction of 2-trimethylsilylpyridine with benzaldehyde[13].

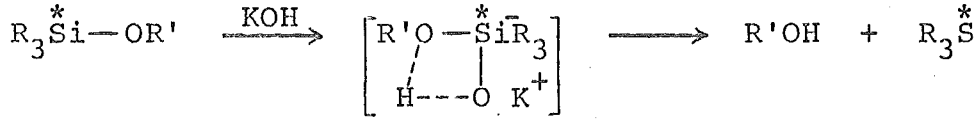


Retention of configuration also predominates in the alkali cleavage of other methyl 1-napthylphenylsilyl derivatives[56].

$$R_3^*Si-OR' \xrightarrow{KOH} R_3^*Si-O^-K^+ + R'-OH$$

(R' = Me, ^{t}Bu, cyclohexyl)

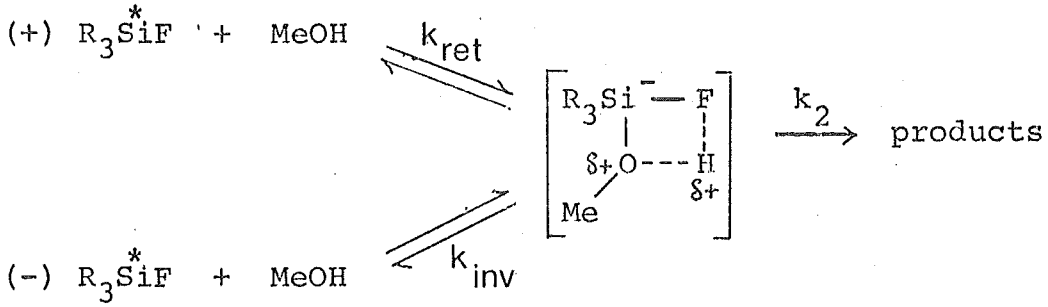
As in the previous reaction, the electrophilic portion of the reagent could assist the leaving group, if flank attack at silicon occurs:



The rule which has evolved for the stereochemistry of substitution at silicon states that "reactions carried out in non-polar solvents and involving poor leaving groups (pK_a conjugate acid of leaving group >10) occur with retention, while reactions involving good leaving groups (pK_a < 6) occur with inversion"[56]. This is consistent with the preceding discussion because in non-polar solvents, the most electrophilic species present which could facilitate substitution by aiding a poor leaving group is the electrophilic portion of the nucleophile, and this is in a sterically favourable

position if flank attack, and consequently retention, occurs. If the leaving group is "good", such electrophilic assistance is not as necessary for reaction, and inversion or retention is possible, as in the hydrolysis of trialkylchlorosilanes, where inversion occurs[57]. Although inversion does occur in the methanolysis of methoxymethyl 1-napthylphenylsilane[58], which contains a poor leaving group, (MeO-), this can be explained, because the reaction is carried out in a polar solvent, which, being identical to the nucleophile, can give electrophilic assistance to the leaving group so that flank attack is not necessary.

So although inversion is consistent with an S_N2 mechanism, it can be rationalized with intermediate formation; it is more difficult to rationalize retention with an S_N2 mechanism. Strong evidence in favour of intermediate formation is the racemization of trialkylfluorosilanes in methanol without loss of fluorine[59]. Racemization is thought to occur via equilibrium formation of an intermediate as follows:



where $k_{ret} \sim k_{inv} > k_2$.

If a trigonal bipyramidal intermediate is formed, the nucleophile must occupy an equatorial position, (Fig. 3(a)), if its loss is to result in both inversion and retention. Rear attack is ruled out; the nucleophile cannot occupy an axial position as its loss would give retention only. If a tetra-

gonal pyramid intermediate is formed, both inversion and retention are most likely if the nucleophile occupies the axial position (Fig. 3(b)).

(a) (b)

Fig. 3

Most evidence suggests that intermediate formation is rapid. Triphenylchlorosilane hydrolyses more rapidly than triphenylfluorosilane[60]; although consistent with an S_N2 mechanism, this is also consistent with a mechanism in which decomposition of intermediate to products is rate determining, as chloride ion is a better leaving group than fluoride ion. One would expect the reverse order if intermediate formation was rate determining, as the more electronegative fluorine should make silicon more susceptible to nucleophilic attack. Similarly, the substituted benzyltrimethylsilanes and -stannanes cleave more rapidly than the corresponding phenyltrimethylsilanes and -stannanes. If intermediate formation was rate determining one would expect the reverse order, because the phenyl group could better stabilize negative charge developed on the metal atom by both (d-p)π overlap and inductive effects[61].

Hence, taken overall, evidence favours intermediate formation, probably in a rapid equilibrium step.

(ii) Carbanion formation

As mentioned earlier, the pK_a of a hydrocarbon RH can be taken as a measure of the stability of the carbanion R^-. For relatively acidic hydrocarbons ($pK_a < 35$) there is reasonable correlation between the logarithms of the rate constants for alkali cleavage of $RSiMe_3$ (e.g. R = PhC ≡ C, 9-fluorenyl, Ph_3C) and the pK_a of the corresponding hydrocarbons RH, suggesting that carbanion formation is involved[11]. However, the rate constants for the cleavage of benzyltrimethylsilane and especially phenyltrimethylsilane do not correlate with the hydrocarbon pK_as , indicating that these reactions may involve a different mechanism. This is reinforced by the isotope effects observed in the cleavage of some trimethylsilyl derivatives. A value of $k_H/k_D \sim 1$ is interpreted as meaning that bond breaking and formation involving hydrogen is not significant in the rate determining step; i.e. a free carbanion is formed which non-selectively picks up a proton from solvent in a subsequent fast step. Conversely $k_H/k_D >> 1$ indicates that bond breaking and formation involving hydrogen occurs to some extent in the rate determining step; i.e. a free carbanion does not develop, because a proton from the solvent assists the leaving group to separate. In the alcoholysis of 2-trimethylsilyl pyridine, k_H/k_D is 1.25[12]; claimed to be close enough to 1 to indicate substantial carbanion formation in the slow step, and consistent with the low pK_a of pyridine (5.2) which implies a stable carbanion. However, for alkali cleavage, $k_H/k_D \sim 1.4$ for benzyltrimethylsilane, and ~ 2.8 for benzyltrimethylstannane. No data is available for phenyltrimethylsilane, but for phenyltrimethylstannane $k_H/k_D \sim 4.4$[62]. These results show

that participation by the solvent is important in the rate determining step, and in the phenyl-metal case at least, the high value of k_H/k_D eliminates the possibility of a free carbanion. The small isotope effect in benzyl-metal cleavage compared with phenyl-metal cleavage shows that more carbanion character is developed in the slow step of the former, and this is reflected in the greater sensitivity to substituent changes in the cleavage of benzyltrimethylsilanes and -stannanes. For alkali cleavage of phenyltrimethylstannanes $\rho = 2.18$ for meta substituents[61], for benzyltrimethylstannanes $\rho = 4.23$[63], and for benzyltrimethylsilanes $\rho = 4.88$[14].

Hence whether or not a free carbanion is formed depends largely on the stability of the incipient carbanion; in phenyl-silicon bond cleavage, free carbanion formation is unlikely.

SUMMARY

For nucleophilic substitution at silicon and other Group IVb metals, the evidence so far available favours initial rapid equilibrium formation of a pentacovalent intermediate utilizing the d-orbitals of the metal atom, followed by its decomposition to products. The latter could occur either in a single rate determining step involving abstraction of a proton from solvent by the leaving group (mechanism a(i)) or, at the other extreme (if the leaving group is sufficiently stable) rate determining separation of the leaving group which abstracts a proton from solvent in a subsequent fast step (mechanism b(i)). The alkali cleavage of the substituted phenyltrimethylsilanes studied in this work is the first comprehensive study of nucleophilic cleavage

of the phenyl-silicon bond and might be expected to follow the former path, i.e. mechanism a(i).

RESULTS

The kinetic data obtained is summarized in the following tables. Pseudo first order rate constants k_p (min^{-1}) and their standard errors σ (min^{-1}) were calculated by a suitably modified ORGLS least squares program. The standard deviation $\bar{\sigma}$ (min^{-1}) in the estimate of the mean rate constant $\bar{k}_p$ (min^{-1}) was calculated using

$$\bar{\sigma} = \left[\frac{\Sigma(\bar{k}_p - k_p)^2}{N(N-1)}\right]^{\frac{1}{2}} \qquad (4)$$

where N is the number of measurements of k_p.

Table 5

Rate Constants for KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO at 40.0°C

X	Wavelength (nm)	$[OH^-]$ (M)	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$
m-NO_2	313	0.02	5.63	0.26		
			5.67	0.17	5.72	0.05
			5.72	0.16		
			5.85	0.17		
p-NO_2	290	0.02	4.40	0.11		
			4.43	0.15	4.46	0.04
			4.45	0.20		
			4.57	0.16		
m-Br	270.5	0.02	0.317	0.004		
			0.320	0.004	0.320	0.002
			0.320	0.004		
			0.325	0.003		
		0.05	0.891	0.014		
			0.897	0.012	0.898	0.002
			0.901	0.015		
			0.905	0.011		
m-CF_3	274	0.05	0.581	0.004		
			0.584	0.004	0.593	0.005
			0.595	0.004		
			0.598	0.004		
			0.608	0.003		
m-Cl	270	0.05	0.478	0.006		
			0.493	0.004	0.491	0.007
			0.502	0.007		
		0.10	0.784	0.007		
			0.788	0.008	0.798	0.008
			0.802	0.008		
			0.818	0.006		
m-F	271.8	0.10	0.217	0.002		
			0.218	0.003	0.218	0.000
			0.218	0.002		

p-Br	272	0.10	0.100 0.000 0.103 0.001 0.103 0.001	0.102 0.001
		0.20	0.148 0.002 0.151 0.001 0.157 0.002	0.152 0.002
p-Cl	274	0.20	0.103 0.002 0.104 0.003 0.105 0.002	0.104 0.001
p-F	270.2	0.20	$(2.39 \pm 0.02) \times 10^{-2}$ $(2.44 \pm 0.02) \times 10^{-2}$	$(2.41 \pm 0.03) \times 10^{-2}$
m-Ph	290	0.20	$(1.14 \pm 0.02) \times 10^{-2}$ $(1.15 \pm 0.01) \times 10^{-2}$ $(1.17 \pm 0.02) \times 10^{-2}$	$(1.15 \pm 0.01) \times 10^{-2}$
p-Ph	276	0.20	$(7.36 \pm 0.07) \times 10^{-3}$ $(7.53 \pm 0.11) \times 10^{-3}$ $(7.57 \pm 0.18) \times 10^{-3}$	$(7.49 \pm 0.06) \times 10^{-3}$
m-OMe	285	0.20	$(6.35 \pm 0.06) \times 10^{-3}$ $(6.45 \pm 0.08) \times 10^{-3}$ $(6.75 \pm 0.07) \times 10^{-3}$	$(6.52 \pm 0.12) \times 10^{-3}$
H	270.5	0.20	$(2.96 \pm 0.04) \times 10^{-3}$ $(3.02 \pm 0.05) \times 10^{-3}$ $(3.03 \pm 0.04) \times 10^{-3}$	$(3.00 \pm 0.02) \times 10^{-3}$
m-Me	275	0.20	$(1.35 \pm 0.03) \times 10^{-3}$ $(1.37 \pm 0.03) \times 10^{-3}$ $(1.38 \pm 0.04) \times 10^{-3}$	$(1.37 \pm 0.01) \times 10^{-3}$
p-Et	274	0.20	$(1.19 \pm 0.04) \times 10^{-3}$ $(1.23 \pm 0.04) \times 10^{-3}$	$(1.21 \pm 0.02) \times 10^{-3}$
p-Me	274	0.20	$(7.80 \pm 0.19) \times 10^{-4}$ $(7.89 \pm 0.21) \times 10^{-4}$ $(8.10 \pm 0.18) \times 10^{-4}$	$(7.93 \pm 0.09) \times 10^{-4}$
p-OMe	285	0.20	$(7.04 \pm 0.11) \times 10^{-4}$ $(7.10 \pm 0.15) \times 10^{-4}$ $(7.12 \pm 0.12) \times 10^{-4}$	$(7.09 \pm 0.03) \times 10^{-4}$

m-NMe_2	274	0.20	$(3.75 \pm 0.36) \times 10^{-4}$ $(4.15 \pm 0.30) \times 10^{-4}$	$(3.95 \pm 0.20) \times 10^{-4}$
p-NMe_2	290	0.20	$(8.39 \pm 0.39) \times 10^{-5}$ $(7.29 \pm 0.35) \times 10^{-5}$	$(7.84 \pm 0.55) \times 10^{-5}$

Table 6

Overlap Factors for KOH Cleavage of $XC_6H_4SiMe_3$ in ⊥0% v/v H_2O/DMSO at 40.0°C

X	$[OH^-]$ (M)	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$	overlap factor $\bar{k}_p$ (0.05M)/$\bar{k}_p$ (0.02M)
m-Br	0.02	0.317	0.004			
		0.320	0.004	0.320	0.002	2.80 ∓ 0.07
		0.320	0.004			
		0.325	0.003			
	0.05	0.891	0.014			
		0.897	0.012	0.898	0.002	
		0.901	0.015			
		0.905	0.011			
m-CF_3	0.02	0.209	0.001			
		0.220	0.001	0.218	0.005	
		0.224	0.001			
	0.05	0.581	0.004			2.72 ∓ 0.25
		0.584	0.004			
		0.595	0.004	0.593	0.005	
		0.598	0.004			
		0.608	0.003			

Table 7

Rate Constants for KOH Cleavage of Heterocyclic Aryltrimethylsilanes ($ArSiMe_3$) at 40.0°C

Ar-	λ (n.m.)	solvent	$[OH^-]$	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$
3-thienyl-	258	10% H_2O/DMSO	0.20	0.273	0.001	0.278	0.002
				0.278	0.002		
				0.279	0.002		
				0.282	0.001		
		33% H_2O/DMSO	0.60	$(7.14 \pm 0.27) \times 10^{-4}$		$(7.22 \pm 0.04) \times 10^{-4}$	
				$(7.25 \pm 0.23) \times 10^{-4}$			
				$(7.27 \pm 0.34) \times 10^{-4}$			
p-$NO_2C_6H_4$-	290	33% H_2O/DMSO	0.60	$(2.93 \pm 0.08) \times 10^{-2}$		$(2.94 \pm 0.01) \times 10^{-2}$	
				$(2.95 \pm 0.08) \times 10^{-2}$			
m-$NO_2C_6H_4$-	313	33% H_2O/DMSO	0.60	$(4.29 \pm 0.07) \times 10^{-2}$		$(4.38 \pm 0.10) \times 10^{-2}$	
				$(4.48 \pm 0.05) \times 10^{-2}$			
2-thienyl-	263	33% H_2O/DMSO	0.60	0.938	0.006	0.964	0.012
				0.952	0.009		
				0.978	0.007		
				0.988	0.010		
		50% MeOH/DMSO	0.50	$(2.49 \pm 0.02) \times 10^{-2}$		$(2.49 \pm 0.02) \times 10^{-2}$	
	n.m.r.	50% MeOH/DMSO	0.50	$(2.37 \pm 0.05) \times 10^{-2}$		$(2.40 \pm 0.03) \times 10^{-2}$	
				$(2.43 \pm 0.07) \times 10^{-2}$			
2-furyl-	n.m.r.	50% MeOH/DMSO	0.50	$(3.05 \pm 0.11) \times 10^{-3}$		$(3.10 \pm 0.05) \times 10^{-3}$	
				$(3.15 \pm 0.11) \times 10^{-3}$			

Table 8

Rate Constants for Cleavage of $ArSiMe_3$ by 0.05M KOH in Varying H_2O/DMSO Mixtures at 40.0°C

% DMSO (v/v)	mole % DMSO	Ar	k_p σ	$\bar{k}_p$ $\bar{\sigma}$
66.67	33.40	2-thienyl	$(5.38 \pm 0.03) \times 10^{-2}$ $(5.47 \pm 0.05) \times 10^{-2}$ $(5.58 \pm 0.03) \times 10^{-2}$	$(5.48 \pm 0.06) \times 10^{-2}$
75	42.94	2-thienyl	$(4.45 \pm 0.04) \times 10^{-1}$ $(4.48 \pm 0.03) \times 10^{-1}$ $(4.49 \pm 0.02) \times 10^{-1}$ $(4.50 \pm 0.02) \times 10^{-1}$	$(4.48 \pm 0.01) \times 10^{-1}$
		p-$NO_2C_6H_4$	$(1.81 \pm 0.02) \times 10^{-2}$	$(1.81 \pm 0.02) \times 10^{-2}$
77.5	46.35	2-thienyl	$(9.35 \pm 0.08) \times 10^{-1}$ $(9.44 \pm 0.09) \times 10^{-1}$ $(9.97 \pm 0.11) \times 10^{-1}$	$(9.59 \pm 0.19) \times 10^{-1}$
		p-$NO_2C_6H_4$	$(4.32 \pm 0.04) \times 10^{-2}$ $(4.63 \pm 0.04) \times 10^{-2}$	$(4.48 \pm 0.16) \times 10^{-2}$
80	50.09	2-thienyl	2.02 . 0.01 2.09 . 0.01 2.10 . 0.01	2.07 . 0.03
		p-$NO_2C_6H_4$	$(1.17 \pm 0.01) \times 10^{-1}$ $(1.17 \pm 0.01) \times 10^{-1}$ $(1.19 \pm 0.01) \times 10^{-1}$	$(1.18 \pm 0.01) \times 10^{-1}$
85	58.70	p-$NO_2C_6H_4$	$(9.11 \pm 0.07) \times 10^{-1}$ $(9.31 \pm 0.08) \times 10^{-1}$ $(9.65 \pm 0.07) \times 10^{-1}$	$(9.36 \pm 0.16) \times 10^{-1}$
		m-FC_6H_4	$(1.35 \pm 0.03) \times 10^{-2}$	$(1.35 \pm 0.03) \times 10^{-2}$
86.67	61.99	p-$NO_2C_6H_4$	2.16 . 0.02 2.23 . 0.02 2.26 . 0.02	2.22 . 0.03
		m-FC_6H_4	$(2.79 \pm 0.02) \times 10^{-2}$	$(2.79 \pm 0.02) \times 10^{-2}$

90	69.30	m-FC_6H_4	$(1.31 \pm 0.01) \times 10^{-1}$ $(1.35 \pm 0.02) \times 10^{-1}$ $(1.39 \pm 0.02) \times 10^{-1}$	$(1.35 \pm 0.02) \times 10^{-1}$
92	74.26	m-FC_6H_4	$(4.95 \pm 0.06) \times 10^{-1}$ $(5.01 \pm 0.05) \times 10^{-1}$ $(5.04 \pm 0.04) \times 10^{-1}$	$(5.00 \pm 0.03) \times 10^{-1}$
		p-FC_6H_4	$(3.99 \pm 0.04) \times 10^{-2}$	$(3.99 \pm 0.04) \times 10^{-2}$
94	79.72	m-FC_6H_4	1.41 ± 0.01 1.41 ± 0.01 1.46 ± 0.01	1.42 ± 0.03
		p-FC_6H_4	$(1.21 \pm 0.01) \times 10^{-1}$ $(1.23 \pm 0.01) \times 10^{-1}$	$(1.22 \pm 0.01) \times 10^{-1}$
95	82.66	m-FC_6H_4	2.44 ± 0.02 2.54 ± 0.02 2.59 ± 0.04	2.52 ± 0.04
		p-FC_6H_4	$(2.28 \pm 0.02) \times 10^{-1}$ $(2.30 \pm 0.02) \times 10^{-1}$	$(2.29 \pm 0.01) \times 10^{-1}$
96	85.76	p-FC_6H_4	$(3.89 \pm 0.02) \times 10^{-1}$ $(4.01 \pm 0.03) \times 10^{-1}$ $(4.03 \pm 0.02) \times 10^{-1}$	$(3.98 \pm 0.04) \times 10^{-1}$
97	89.02	p-FC_6H_4	$(6.11 \pm 0.04) \times 10^{-1}$ $(6.19 \pm 0.05) \times 10^{-1}$ $(6.23 \pm 0.04) \times 10^{-1}$	$(6.18 \pm 0.04) \times 10^{-1}$
97.5	90.73	p-FC_6H_4	0.979 ± 0.007 0.989 ± 0.011 1.01 ± 0.01 1.04 ± 0.01	1.00 ± 0.01

Table 9

Rate Constants for KOH Cleavage of 2-Thienyltrimethylsilane in $33\frac{1}{3}$% v/v H_2O/DMSO at 40.0°C

$[OH^-]$ (M)	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$
0.60	0.938	0.006		
	0.952	0.009	0.964	0.012
	0.978	0.007		
	0.988	0.010		
0.40	0.570	0.005		
	0.574	0.004		
	0.575	0.005	0.576	0.002
	0.579	0.005		
	0.580	0.004		
0.20	0.245	0.002		
	0.245	0.002	0.247	0.002
	0.248	0.002		
	0.251	0.002		
0.10	0.119	0.001		
	0.119	0.001	0.119	0.001
	0.119	0.001		
	0.121	0.001		
0.05	$(6{\cdot}08, 0{\cdot}003) \times 10^{-2}$		$(6{\cdot}08, 0{\cdot}003) \times 10^{-2}$	

Table 10

Cleavage of 2-Thienyltrimethylsilane by Various Nucleophiles in DMSO[a]

Nucleophile X^-	pK_a HX	[X] (M)	T(°C)	Time (hrs)	% reaction	approx. half-life (hours)	product signal[b] (cps)
OH^-	15.74	1.0	40	0.1	100	<0.02	-28
MeO^-	15.5	1.0	40	0.1	100	<0.02	-28
NH_2^-	>16	1.0	40	0.1	100	<0.02	-13,-30
H^-	>16	1.0	40	6.5	40	9	-13
PhO^-	9.89	1.0	40	6.5	40	9	-13,-15
CN^-	9.31	0.1	40	300	7	2500	-15
I^-	0.77	0.1	40	300	0	-	
Cl^-	<0	1.0	70	40	0	-	
Br^-	<0	1.0	70	40	0	-	
N_3^-	4.62	0.25	70	40	0	-	
SCN^-	-1.38	1.0	70	40	0	-	
NEt_3	11.01	1.0	70	40	0		

[a] monitored by n.m.r.

[b] position of product trimethylsilyl signal relative to reactant signal

Table 11

Cleavage of 2-Thienyltrimethylsilane by Various Nucleophiles in 10% v/v H_2O/DMSO at 40.0°C [a]

Nucleophile X^- (0.2M)	pK_{HX} [a]	% reaction at: 12 hrs	90 hrs	240 hrs	1200 hrs	approx. half-life (hrs)	product signal [b] (cps)
OH^-	15.8	100				<3	-28
O_2^{2-}	11.62	100				<3	-28
F^-	3.45	86	100			4	-14,-15
CN^-	9.31	12	85	100		35	-14,-15
SiO_3^{2-}	9.66	-	19	59	100	200	-14,-15
OCl^-	7.53	-	5	13	77	600	-14,-15
NH_3	9.25	-	-	4	12	5000	-15
AcO^-	4.75	-	-	< 2	4	>> 1200	-15

The following nucleophiles X^- (pK_a of HX in brackets) showed no sign of reaction after 1200 hours; triethylamine (11.01), S^{2-} (7.04), pyridine (5.25), aniline (4.63), NO_2^- (3.37), SO_3^{2-} (1.81), I^- (0.77), pyrrole (-3.80) and 2,4-dinitroaniline (-4.53).

[a] monitored by n.m.r.

[b] position of product trimethylsilyl peak relative to the reactant signal.

Table 12

Rate Constants for KOH Cleavage of $XC_6H_4SiMe_3$ in 5% v/v MeOH/DMSO at 40.0°C

X	$[OH^-]$	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$	$k_{rel.}$	(∓) error
m-NO_2	0.03	1.34	0.02	1.37	0.02	27.2	3
		1.36	0.02				
		1.40	0.03				
p-NO_2	0.03	1.24	0.01	1.26	0.01	25.0	2
		1.25	0.01				
		1.28	0.01				
m-Br	0.03	$(5.04 \pm 0.07) \times 10^{-2}$		$(5.04 \pm 0.07) \times 10^{-2}$		1.00	0.02
	0.10	0.432	0.005	0.435	0.003		
		0.438	0.012				
m-CF_3	0.10	0.340	0.003	0.340	0.000	0.781	0.020
		0.340	0.004				
m-Cl	0.10	0.255	0.002	0.259	0.003	0.595	0.030
		0.262	0.002				
m-F	0.10	$(7.41 \pm 0.06) \times 10^{-2}$		$(7.50 \pm 0.09) \times 10^{-2}$		0.172	0.010
		$(7.60 \pm 0.05) \times 10^{-2}$					
p-Br	0.10	$(5.03 \pm 0.08) \times 10^{-2}$		$(5.03 \pm 0.08) \times 10^{-2}$		0.116	0.008
p-Cl	0.10	$(2.40 \pm 0.13) \times 10^{-2}$		$(2.40 \pm 0.13) \times 10^{-2}$		0.0552	0.010

Table 13

Rate Constants for MeONa Cleavage of m-$BrC_6H_4SiMe_3$ in 5% v/v MeOH/DMSO at 40.0°C

$[MeO^-]$ (M)	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$
0.25	0.521	0.010	0.527	0.007
	0.534	0.011		
0.20	0.340	0.009	0.340	0.000
	0.340	0.011		
0.10	0.152	0.003		
	0.153	0.005	0.154	0.002
	0.157	0.002		
0.03	$(3.05 \pm 0.03) \times 10^{-2}$		$(3.05 \pm 0.03) \times 10^{-2}$	

Table 14

Rate Constants for MeONa Cleavage of $XC_6H_4SiMe_3$ in 5% v/v MeOH/DMSO at 40.0°C

X	$[MeO^-]$	k_p	σ	$\bar{k}_p$	$\bar{\sigma}$	$k_{rel.}$	$\pm$ error
m-NO_2	0.03	0.848	0.005				
		0.868	0.009	0.864	0.009	28.3	3.1
		0.877	0.015				
p-NO_2	0.03	0.758	0.006				
		0.762	0.006	0.772	0.012	25.3	3.2
		0.797	0.007				
m-Br	0.03	(3.05 . 0.04) x 10^{-2}		(3.05 . 0.04) x 10^{-2}			
	0.25	0.521	0.010	0.527	0.007	1.00	0.04
		0.534	0.011				
m-CF_3	0.25	0.361	0.006	0.362	0.001	0.686	0.033
		0.362	0.004				
m-Cl	0.25	0.278	0.002	0.289	0.012	0.549	0.091
		0.301	0.003				
m-F	0.25	(8.33 . 0.05) x 10^{-2}		(8.60 . 0.28) x 10^{-2}		0.163	0.081
		(8.88 . 0.11) x 10^{-2}					
	0.27	(8.81 . 0.17) x 10^{-2}		(9.63 . 0.82) x 10^{-2}			
		0.105	0.003				
p-Br	0.27	(6.71 . 0.19) x 10^{-2}		(6.71 . 0.19) x 10^{-2}		0.114	0.042

DISCUSSION

SUBSTITUENT EFFECTS IN THE KOH CLEAVAGE OF $XC_6H_4SiMe_3$ IN 10% v/v H_2O/DMSO

A series of substituted phenyltrimethylsilanes was synthesized and rates of KOH cleavage in 10% v/v H_2O/DMSO measured spectrophotometrically at 40.0°C. The reactions are first order in silane and were carried out in pseudo first order conditions, i.e. $[OH^-] \geqslant 10[ArSiMe_3]$.

The pseudo first order rate constants were derived from the data using a modified ORGLS least squares program and were reproducible (see Table 5).

However, because of the wide range of reactivity encountered, rate constants could not all be measured at the same KOH concentration. To derive the set of relative pseudo first order rate constants (k_{rel}) for the series, rate constants for the cleavage of the m-Br, m-Cl and p-Br substituted compounds were determined at two different KOH concentrations and overlapping used to relate the results. Overlapping involves the assumption that the rate dependence on hydroxide concentration is independent of the substituent present in the substrate. This was verified by determining rate constants for both m-CF_3 and m-Br in 0.02M KOH and 0.05M KOH media. As Table 6 shows the overlap factor (relative change in k_p between the two concentrations) is reproducible. Because of the three overlapping steps required to derive k_{rel}, errors accumulate; hence the high error (22%) in the value for m-NO_2 (see table 15).

Table 15

Substituent Effects in KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO at 40.0°C

X	$k_{rel.}$	(∓)error[a]	log $k_{rel.}$	(∓)error
m-NO_2	13000	2800	4.11	0.10
p-NO_2	10100	2200	4.00	0.10
m-Br	726	120	2.86	0.08
m-CF_3	479	90	2.68	0.09
m-Cl	397	47	2.60	0.06
m-F	108	10	2.03	0.04
p-Br	50.7	3.0	1.70	0.03
p-Cl	34.7	1.7	1.54	0.02
p-F	8.03	0.46	0.905	0.017
m-Ph	3.83	0.18	0.583	0.020
p-Ph	2.50	0.06	0.398	0.010
m-OMe	2.17	0.16	0.337	0.032
H	1.00	0.02	0.000	0.008
m-Me	0.457	0.019	-0.340	0.018
p-Et	0.403	0.028	-0.395	0.030
p-Me	0.264	0.014	-0.578	0.023
p-OMe	0.236	0.008	-0.627	0.014
m-NMe_2	0.132	0.023	-0.879	0,080
p-NMe_2	0.0261	0.006	-1.58	0.10

[a] The relationship: error = $3\bar{\sigma}$ is used to estimate the error in $\bar{k}_p$ values used for determining the relative rate constants.

Correlations between these results and various substituent constant scales were investigated using a modified ORGLS least squares program which could fit data to any of four linear equations:

$$P = \rho\sigma' \quad (5)$$

$$P = \rho\sigma' + c \quad (6)$$

$$P = \rho(\sigma' + r\sigma'') \quad (7)$$

$$P = \rho(\sigma' + r\sigma'') + c \quad (8)$$

P is the substituent parameter (k_{rel}), ρ is the slope of the line, and σ', σ'' are substituent constants; c is the intercept if the correlation is not constrained through the origin. The relationships investigated were:

(i) Hammett equation (via equation (6))

$$\log k_{rel} = \rho\sigma' + c.$$

(ii) Yukawa-Tsuma equation (via equation (8))

$$\log k_{rel} = \rho(\sigma' + r\sigma'') + c$$

(iii) Dual parameter equation (via equation (7))

$$\log k_{rel} = \rho_I(\sigma_I + \lambda\sigma_R^{x})$$

The concepts involved in (ii) and (iii) will be more fully discussed later.

It has been suggested[64] that correlations of good precision are those for which

$$f = \frac{S.D.}{R.M.S.} \leqslant 0.1 \quad (9)$$

where R.M.S. and S.D. are the root mean square values of the substituent parameters, and their deviations respectively.

$$\text{R.M.S.} = \left(\frac{\sum_{i=1}^{N} (P^i_{obs})^2}{N} \right)^{\frac{1}{2}} \qquad (10)$$

$$\text{S.D.} = \left(\frac{\sum_{i=1}^{N} (P^i_{obs} - P^i_{calc})^2}{N} \right)^{\frac{1}{2}} \qquad (11)$$

P^i_{obs}, P^i_{calc} are the observed and calculated values of the parameters of the i^{th} substituent, and N is the number of substituents in the correlation. This measure of correlation has been adopted here not only for convenience ($\sum_{i=1}^{N} (P^i_{obs}-P^i_{calc})^2$ is one of the variables in the least squares procedure, and calculated by the program), but also because it is considered to be superior to the more conventional correlation coefficient which often places both good and poor correlations between 0.9 - 1.0. Correlations involving the Hammett and Yukawa-Tsuno equations were not constrained through the origin, although constraint did not significantly increase f values. Correlations involving the Dual parameter equation were constrained, as suggested by Taft[64].

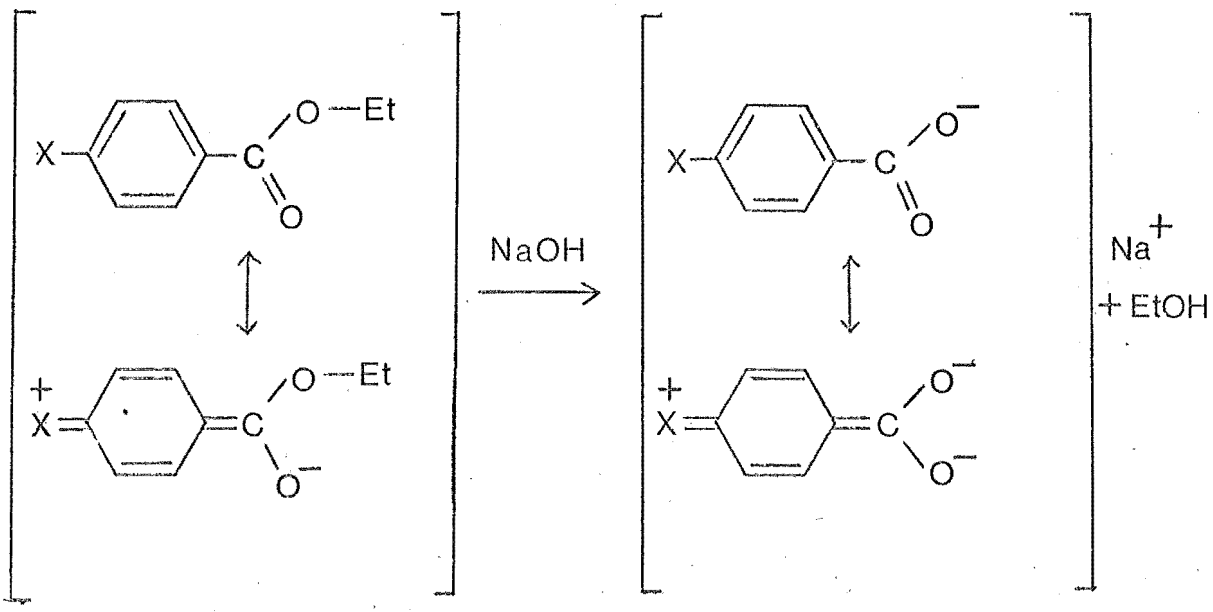
As a basis of discussion, the σ^0 scale suggested by Taft[65] has been adopted, rather than the σ scale originally suggested by Hammett. The σ^0 substituent constants are based on reactions such as the ionization of phenylacetic and phenylpropionic acids - species in which the reaction site is insulated from direct resonance with the aromatic ring by one or more methylene groups. The σ^0 scale is useful for correlating reactions in which

(i) there is no direct conjugation between substituent

and reaction site, and

(ii) the resonance and inductive effects of a substituent have the same relative importance in both ground and transition state.

Neither condition holds in the reactions used as a basis of the σ scale. For example in the hydrolysis of benzoic esters, direct conjugation occurs between +R substituents in the para position, and the reaction site.



This resonance stabilization is more important in the ester than the anion, probably because of much stronger electron repulsions in the latter. As the transition state contains some anionic character, the resulting stabilization of the ground state relative to the transition state depresses the reaction rate. Consequently, σ values for para +R substituents are lower than expected, as a comparison of σ and σ^0 values shows (see Table 16).

Table 16

Substituent Constants for +R Substituents

Substituent	σ	σ^0
p-NMe_2	-0.83	-0.44
p-F	0.06	0.17
m-F	0.34	0.35
p-OMe	-0.23	-0.16

(i) Correlation with σ

Overall, this correlation is poor (f = 0.263) although there is reasonable correlation (f = 0.121) of the meta points with σ about the straight line

$$\log k_{rel} = 5.88\sigma + 0.14 \quad \text{(Fig. 4)}.$$

The para points are well scattered about the line. All +R substituents lie above it, especially strongly +R groups (p-NMe_2, p-OMe, p-Ph) which deviate significantly. The only -R substituent studied (p-NO_2) deviates significantly below the line.

This correlation, however, is rather misleading, as it is difficult to attach much importance to the deviations of the +R substituents, when σ is used. It could simply indicate that direct conjugation between +R substituents and the reaction site is either absent in the reaction, or not as destabilizing in the transition state.

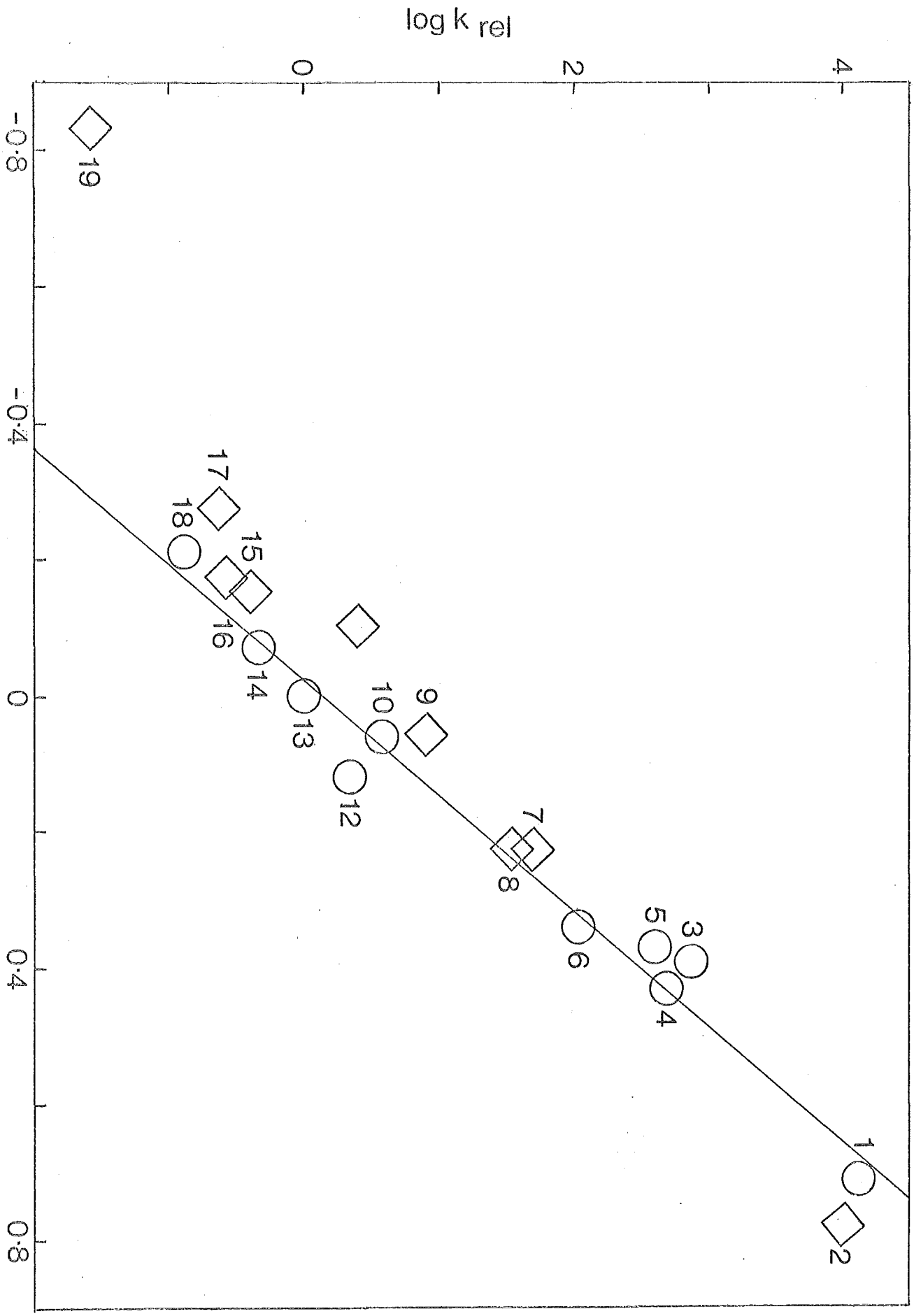


Fig. 4

Log k_{rel} vs σ for the KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO

(ii) Correlation with σ^0

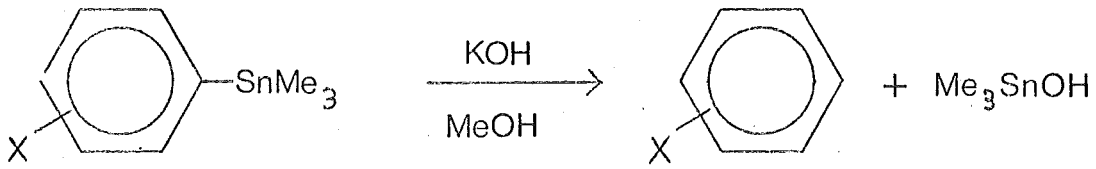
Overall, a better correlation results using σ^0 (f = 0.131) rather than σ (f = 0.263). The meta substituents (except m-Br) correlate quite well with σ^0 about the line

$$\log k_{rel} = 6.08\sigma^0 + 0.12, \qquad (f = 0.100).$$

The deviations of para points about the line are less marked than in the plot against σ; +R substituents (except the halogens) still lie above the line, although only p-NMe_2 deviates significantly. The only -R substituent (p-NO_2) lies below the line (Fig. 5).

Two structurally similar reactions which may also involve a transition state with carbanion-like character on the phenyl ring display a similar pattern of substituent effects. In the first reaction, the cleavage of substituted aryltrimethyl-stannanes in KOH/MeOH[61], the meta points (except m-F) correlate well with σ^0 about the straight line

$$\log k_{rel} = 2.15\sigma^0 + 0.09 \qquad (f = 0.095).$$



The deviations of para +R substituents above this line are very marked; in fact p-OMe and p-NMe_2 are faster than H in this reaction (Fig. 6). In 1:6 v/v H_2O/DMSO, for a limited range of substituents, the meta points also correlate well with σ^0 about the straight line,

$$\log k_{rel} = 4.74\sigma^0 + 0.001 \qquad (f = 0.005)$$

although the deviations of para +R substituents about the line are not as marked as in methanol solvent[66].

Similarly, in base catalysed H-exchange in substituted benzenes[61], meta points correlate well with σ^0 about the straight line

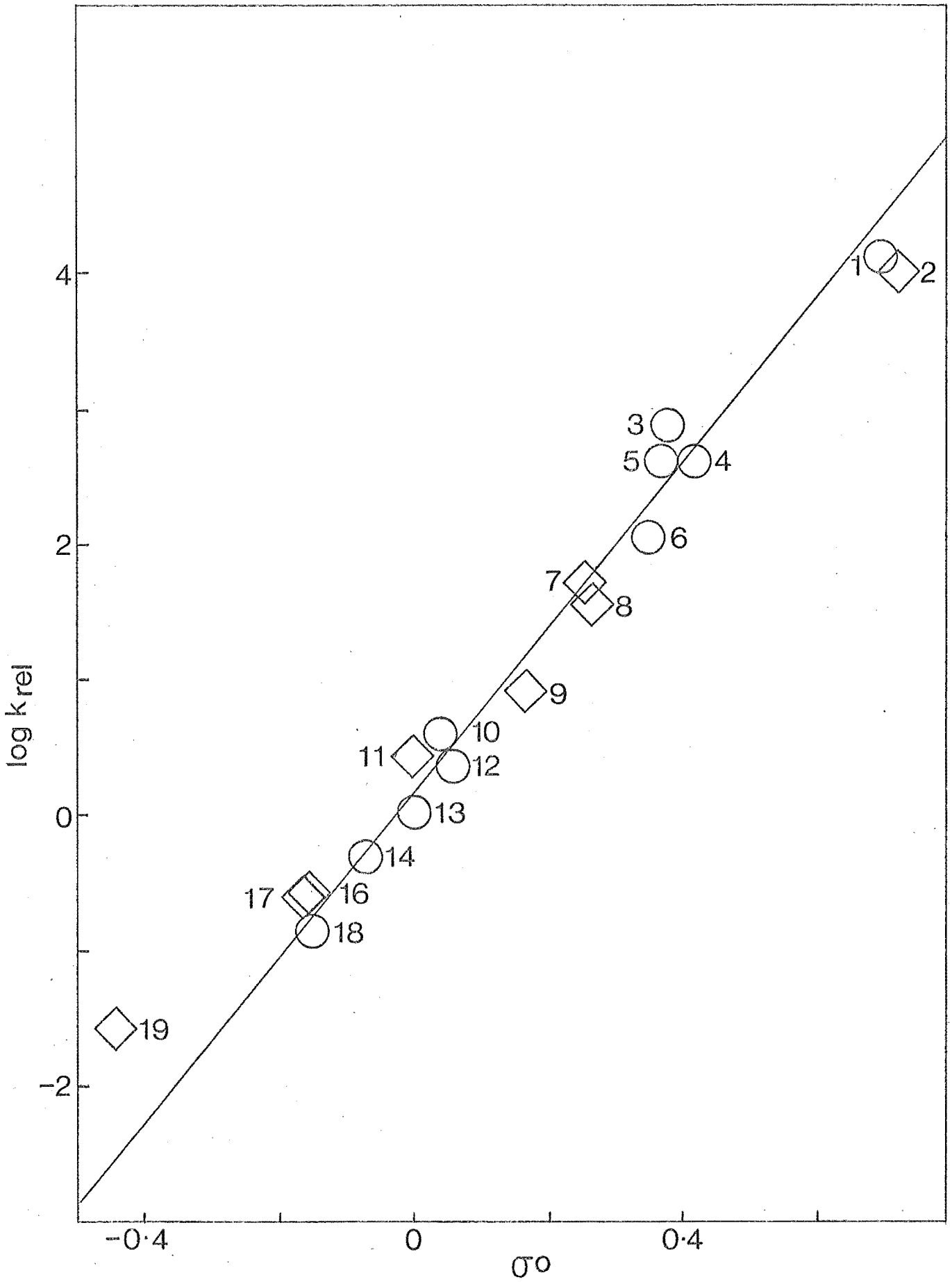


Fig. 5

Log k_{rel} vs σ^0 for the KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO

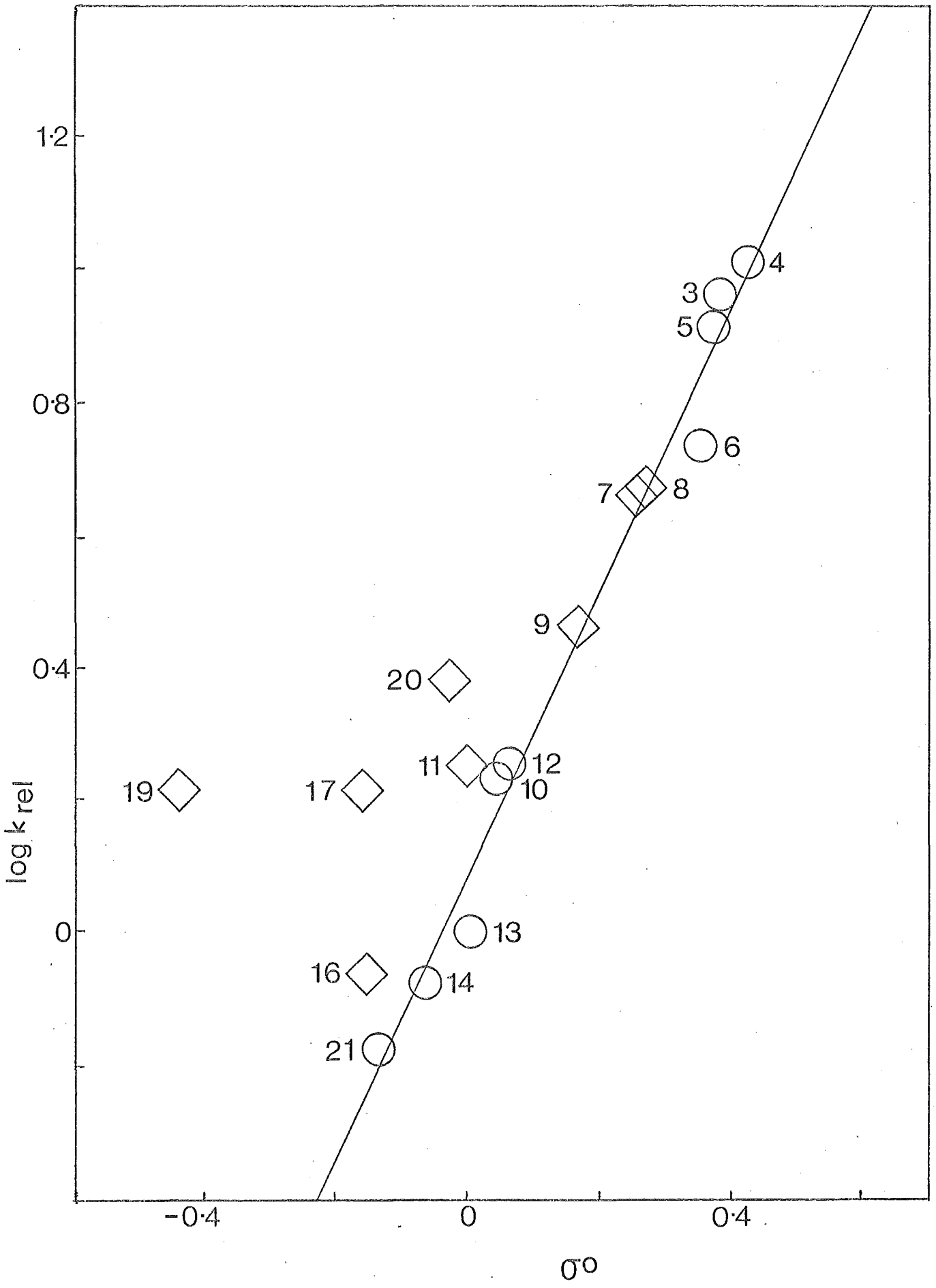


Fig. 6

Log k_{rel} vs σ^0 for the KOH Cleavage of $XC_6H_4SnMe_3$ in MeOH

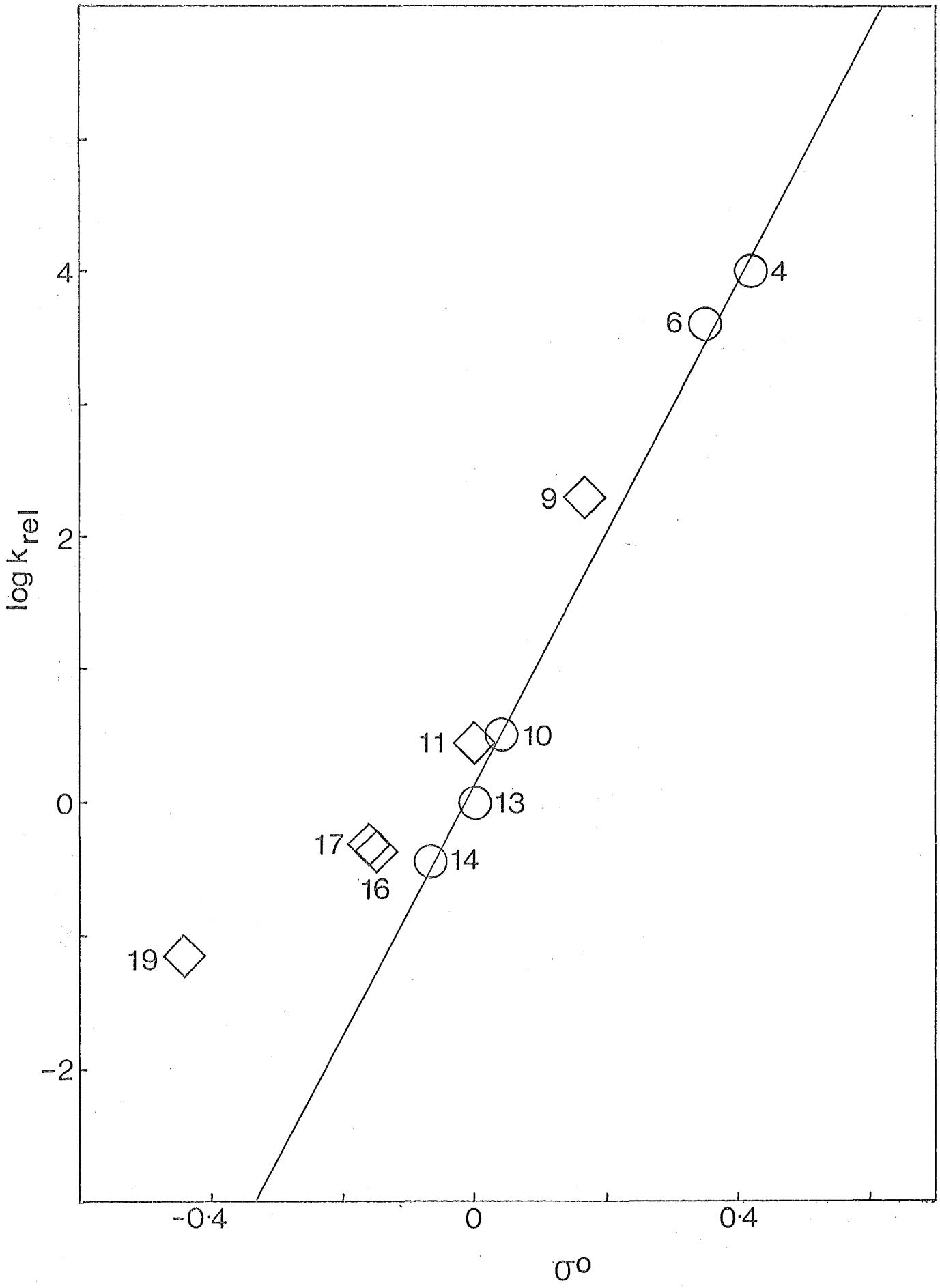


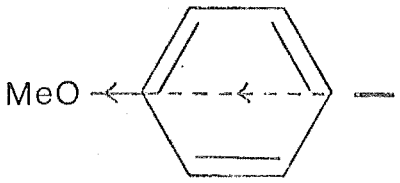
Fig. 7

Log k_{rel} vs σ^0 for Base Catalysed H-Exchange in Substituted Benzenes

$$\log k_{rel} = 9.48\sigma^0 + 0.13 \quad (f = 0.045).$$

The deviations of para +R substituents in this case are of similar magnitude to those in the cleavage of aryltrimethylstannanes in H_2O/DMSO (Fig. 7).

Several explanations have been suggested for the pattern of substituent effects in these reactions. One suggestion, originally put forward to explain the rates of H-exchange in polycyclic aromatics[67], is that since the substituents involved are also inductively electron withdrawing, an inductive field effect stabilizes carbanion character developed in the transition state, e.g.



This explanation is improbable for the following reasons:

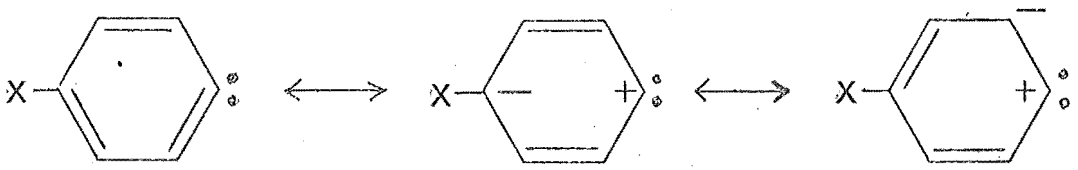
(i) the deviations are restricted to ortho and para substituents; meta substituents correlate well with σ^0. As meta substituents are closer to the reaction site than para, they should deviate even more markedly than para substituents.

(ii) there is no correlation between meta or para substituents and σ_I (see Table 17). Such a correlation would be expected if inductive field effects were strong enough to activate the p-OMe and p-NMe_2 substituted phenyltrimethylstannanes in KOH cleavage.

(iii) the deviations are greater in the cleavage of aryltrimethylstannanes (ρ = 2.15) than in base catalysed H-exchange (ρ = 9.48). The high ρ value in H-exchange indicates greater

carbanion formation in the transition state than in the cleavage of aryltrimethylstannanes, so that greater stabilization by inductive electron withdrawing substituents would be expected for the H-exchange.

Another suggestion is that the deviations arise from the suppression of electron releasing resonance effects normally present in reactions where there is no direct resonance between substituent and reaction site[61]. Although the lone pair in the phenyl carbanion developed in the transition state cannot delocalize through the π system (as it lies in the plane of the ring), it could distort the π electron cloud electrostatically to the extent that negative charge is localized at the ortho and para positions:



The presence of this high π electron density at the para position could suppress the normal electron releasing resonance effect of the substituent. However, this explanation is also unsatisfactory, because again one would expect the deviations of the substituents to increase as the degree of carbanion development in the transition state increases, but the deviations are more marked in the cleavage of aryltrimethylstannanes (ρ = 2.15) than in base catalysed H-exchange (ρ = 9.48).

As has already been shown in the introduction to this discussion, there is evidence that solvent participation occurs

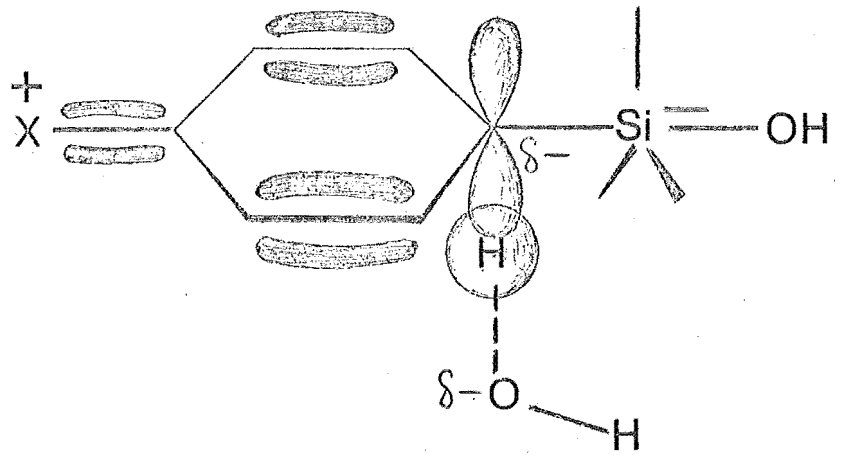
in the rate determining step of reactions bearing close resemblance to the alkali cleavage of aryltrimethylsilanes. Stereochemical evidence is consistent with some form of solvent participation, as in the alcoholysis of (+)2-(methyl 1-napthylphenylsilyl)pyridine[55]. More importantly, isotope effect studies indicate that solvent participation occurs in the rate determining step, rather than in a subsequent step as previously assumed. A large isotope effect (k_H/k_D = 4.4) is observed in the KOH cleavage of phenyltrimethylstannane in MeOH/MeOD[62]. Attempts during the course of this thesis to determine k_H/k_D for the KOH cleavage of phenyltrimethylsilane in DMSO containing H_2O/D_2O were unsuccessful because isotope scrambling between D_2O and DMSO made it impossible to obtain meaningful results. However, for KOH cleavage in MeOH/MeOD[62], k_H/k_D ranged from 1.4 - 1.6 for several substituted benzyltrimethylsilanes, and from 2.0 - 2.8 for similarly substituted benzyltrimethylstannanes, so it would be reasonable to expect a substantial isotope effect for the cleavage of aryltrimethylsilanes.

In reactions such as the KOH cleavage of aryltrimethylsilanes and -stannanes, and base catalysed H-exchange, solvent participation most likely involves overlap by a solvent proton at the central carbon, allowing formation of a C - H bond, and easing the departure of the leaving group.

The following discussion will attempt to show that the patterns of substituent effects in the KOH cleavage of aryltrimethylsilanes, and -stannanes, and base catalysed H-exchange in substituted benzenes, can be explained by a mechanism in which the rate determining step involves separation of a carbanion accompanied by electrophilic assistance from the

solvent.

In all three reactions, ρ is positive, i.e. electron withdrawing substituents enhance and electron releasing substituents retard reaction. This indicates development of negative charge at the reaction site, but is not necessarily evidence of carbanion formation. Electrophilic assistance by solvent and the resulting C - H bond formation should be affected by substituents in a pattern similar to that observed in electrophilic aromatic substitution by H^+, in which the rate determining step also is believed to be C - H bond formation. Substituents will enhance or retard reaction not only by the inductive and resonance effects already described, but also (if para +R substituents are present) by direct conjugative release of electrons by the substituent through the π system to the overlapping vacant s orbital of the proton.

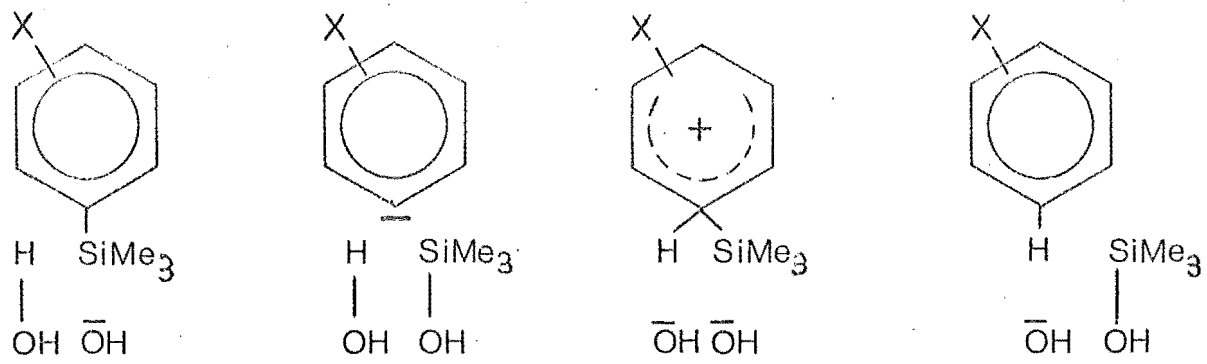


Hence +R substituents such as p-NMe_2, p-OMe, p-Ph should accelerate cleavage by aiding electrophilic attack, even though the reaction is retarded overall through electron release towards the developing carbanion. Such an effect is evident in the results for the cleavage of aryltrimethylsilanes;

para +R substituents (except the halogens) lie above the best fit line through the meta substituents (i.e. are less deactivating than expected). One approach to determining whether this activation is due to conjugative electron release by a substituent is to see if the deviations of the para +R groups from the best fit line correlate with any of the usual yardsticks of conjugative electron release. Although strong +R groups deviate the most, correlations with parameters such as $\sigma^+-\sigma^0$, σ_R^+ [68] are poor. However, correlations between the parameters themselves are poor anyway, and except for p-NMe_2, the deviations of para points from the best fit line through the meta points are relatively small and therefore subject to large errors since the best fit line itself is not very precise (f = 0.100). The same comments hold both for the cleavage of aryltrimethylstannanes, and for base catalysed H-exchange in substituted benzenes; although the deviations are more clear cut, correlations involving the deviations are still poor.

(iii) The Yukawa-Tsuno Equation

If the rate determining step involves separation of a phenyl carbanion accompanied by electrophilic assistance by solvent, four canonical forms I-IV (Fig. 7a) may be written for the transition state, with forms II and III making the major contributions. Since electron withdrawing substituents increase the reaction rate, II predominates and substituent effects should correlate with a suitable substituent constant. However, the enhanced stabilization of III by +R substituents will affect the overall pattern so that the relationship of the type suggested by Yukawa and Tsuno[69] could be used to correlate results;



I II III IV

Fig. 7a

$$\log k_{rel} = \rho(\sigma' + r\Delta\sigma) \qquad (12)$$

where σ' is a substituent constant appropriate for correlating substituent effects on a phenyl carbanion, and $\Delta\sigma$ is a measure of the direct resonance between +R substituents and the reaction site. As σ^+ values incorporate direct resonance between +R substituents and the reaction site, and σ^0 values incorporate no such resonance (apart from that normally operating between a substituent and the phenyl ring), $\sigma^+-\sigma^0$ is used as a suitable parameter for the term $\Delta\sigma$. As Table 18 shows, for the cleavage of p-substituted aryltrimethylsilanes, using $\sigma' = \sigma^0$ and $\Delta\sigma = \sigma^+-\sigma^0$ gives a correlation as good as, or better than, that using other parameters such as $\sigma^+-\sigma$, σ_R, σ_R^0 or σ_R^+.

There are no known reactions solely involving carbanion formation in the transition state on which to base a substituent constant scale. As already shown, base catalysed H-exchange in benzene appears to involve some electrophilic assistance and the acidities of the substituted benzenes are too low to measure. However, reasonable correlations resulted using the σ^0 scale, and somewhat better correlations using the $\bar{\sigma}$ scale[70] (based on

the pK_as of substituted pyridinium ions). The more successful correlations are summarized in Tables 17-22. A discussion of the results, and the merits of the two models follows.

Table 17

Cleavage of $XC_6H_4SiMe_3$: log $k_{rel} = \rho\sigma' + c$

Substituents	n	σ'	ρ	c	f
m	10	σ	5.88	0.14	0.121
	10	σ^+	5.95	0.05	0.101
	10	σ_I	6.41	-0.46	0.261
	10	σ^0	6.08	0.12	0.100
	8	$\bar{\sigma}$	6.15	0.07	0.092
p	9	σ_I	5.45	-0.84	0.519
m,p	19	σ	4.27	0.59	0.263
	18	σ^+	2.51	1.10	0.412
	18	σ^0	5.40	0.26	0.131
	15	$\bar{\sigma}$	5.68	0.29	0.115

n - number of substituents included in the correlation.

Table 18

Cleavage of $XC_6H_4SiMe_3$: $\log k_{rel} = \rho(\sigma' + r\Delta\sigma) + c$

Substituents	n	σ'	$\Delta\sigma$	ρ	r	c	f
m	9	σ	$\sigma^+-\sigma$	6.05	0.600	0.04	0.091
	9	σ_I	$\sigma^+-\sigma_I$	6.03	0.879	0.00	0.098
	9	σ^0	$\sigma^+-\sigma^0$	6.02	0.480	0.09	0.087
	6	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	6.22	2.10	0.09	0.052
p	10	σ	$\sigma^+-\sigma$	4.80	-0.438	0.21	0.198
	8	σ	Δ^-	5.83	0.568	0.11	0.213
	9	σ_I	$\sigma^+-\sigma_I$	4.56	0.316	0.11	0.251
	9	σ^0	$\sigma^+-\sigma^0$	5.32	-0.085	0.10	0.083
	9	σ^0	$\sigma^+-\sigma$	5.27	-0.107	0.12	0.082
	9	σ^0	σ_R	5.07	-0.047	0.19	0.097
	9	σ^0	σ_R^0	5.00	-0.040	0.22	0.099
	9	σ^0	σ_R^+	5.25	0.051	0.11	0.085
	8	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	5.94	-0.185	0.16	0.076
	7	$\bar{\sigma}$	$\sigma^+-\sigma^0$	6.14	-0.094	0.12	0.075
m,p	18	σ	$\sigma^+-\sigma$	5.26	-0.437	0.25	0.191
	17	σ	$\sigma^+-\sigma^0$	5.42	-0.344	0.21	0.168
	17	σ^0	$\sigma^+-\sigma^0$	5.62	-0.073	0.18	0.115
	15	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	6.06	-0.176	0.15	0.095
	15	$\bar{\sigma}$	$\sigma^+-\sigma$	5.96	-0.182	0.16	0.101
	14	$\bar{\sigma}$	$\sigma^+-\sigma^0$	6.06	-0.167	0.13	0.090

Table 19

Cleavage of $XC_6H_4SnMe_3$: $\log k_{rel} = \rho\sigma' + c$

Solvent	Substituents	n	σ'	ρ	c	f
MeOH	m	9	σ	2.32	0.07	0.098
		9	σ^0	2.15	0.09	0.095
		7	$\bar{\sigma}$	2.09	0.06	0.098
		9	σ_I	2.05	-0.10	0.286
	m,p	19	σ	0.863	0.36	0.417
		17	σ^0	1.33	0.29	0.368
		13	$\bar{\sigma}$	1.65	0.20	0.296
H_2O/DMSO	m	3	σ^0	4.74	0.001	0.005
	m,p	7	σ^0	3.53	0.33	0.191

Table 20

Cleavage of $XC_6H_4SnMe_3$: $\log k_{rel} = \rho(\sigma' + r\Delta\sigma) + c$

Solvent	Sub.	n	σ'	$\Delta\sigma$	ρ	r	c	f
MeOH	m,p	15	σ	$\sigma^+-\sigma$	1.95	-0.884	0.12	0.260
		15	σ^0	$\sigma^+-\sigma^0$	2.05	-0.367	0.10	0.149
		12	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	2.04	-0.536	0.08	0.109
		12	$\ddot{\sigma}$	$\sigma^+-\sigma^0$	2.06	-0.472	0.08	0.101
H_2O/DMSO	m,p	7	σ^0	$\sigma^+-\sigma^0$	4.39	-0.187	0.03	0.151
		5	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	4.33	-0.432	-0.02	0.086
		5	$\ddot{\sigma}$	$\sigma^+-\sigma^0$	4.34	-0.368	-0.01	0.093

Table 21

Base Catalysed H-Exchange in Benzene : $\log k_{rel} = \rho\sigma' + c$

Sub.	n	σ'	ρ	c	f
m	5	σ	9.51	0.09	0.072
	5	σ^0	9.48	0.13	0.045
	4	$\bar{\sigma}$	9.27	0.08	0.089
m,p	10	σ	4.32	1.10	0.493
	10	σ^0	6.73	0.76	0.292
	7	$\bar{\sigma}$	6.91	0.537	0.337

Table 22

Base Catalysed H-Exchange in Benzene : $\log k_{rel} = \rho(\sigma' + r\Delta\sigma) + c$

sub.	n	σ'	Δσ	ρ	r	c	f
m,p	10	σ^0	$\sigma^+-\sigma^0$	9.23	-0.217	0.26	0.108
	7	$\bar{\sigma}$	$\sigma^+-\bar{\sigma}$	8.85	-0.338	0.19	0.104
	7	$\bar{\sigma}$	$\sigma^+-\sigma^0$	8.93	-0.297	0.21	0.108

(a) The σ^0 model

In a phenyl carbanion, the central carbon atom remains sp^2 hybridized so that the lone pair of σ electrons of the negative charge lies in the plane of the ring. No direct conjugation can occur between substituents and the lone pair, so that of the accepted substituent constant scales (σ, σ^+, σ^-, σ^0 etc.), the σ^0 scale is the most suitable choice and the equation

$$\log k_{rel} = \rho[\sigma^0 + r(\sigma^+ - \sigma^0)] \qquad (13)$$

can be used to correlate results. For the cleavage of aryltrimethylsilanes, the best fit line is

$$\log k_{rel} = 5.62[\sigma^0 - 0.073(\sigma^+ - \sigma^0)] + 0.18 \qquad \text{(Fig. 8)}$$

As would be expected, r is negative since the enhancing effect of electron supply by +R substituents opposes the otherwise retarding effect of electron supply towards the reaction site. The correlation is reasonable (f = 0.115, compared with 0.131 for $\log k_{rel}$ vs σ^0) and +R substituents (except p-F) lie on the line, although m-Br, m-Cl and p-NO_2 do not.

For aryltrimethylstannane cleavage in methanol and DMSO, the best fit lines are

$$\log k_{rel} = 2.05[\sigma^0 - 0.367(\sigma^+ - \sigma^0)] + 0.10 \quad (f = 0.149)$$

and

$$\log k_{rel} = 4.39[\sigma^0 - 0.187(\sigma^+ - \sigma^0)] + 0.03 \quad (f = 0.151)$$

respectively. Neither correlation is very satisfactory, although both are considerable improvements on simple σ^0 relationships (see Table 19) and para +R substituents lie close to, or on the line in both cases (Fig. 9).

A better Yukawa-Tsuno correlation results for base catalysed H-exchange in benzenes (f = 0.108 compared with f = 0.292 for $\log k_{rel}$ vs σ^0) in which para +R substituents lie on the best fit line

$$\log k_{rel} = 9.23[\sigma^0 - 0.217(\sigma^+ - \sigma^0)] + 0.26 \quad \text{(Fig. 10)}.$$

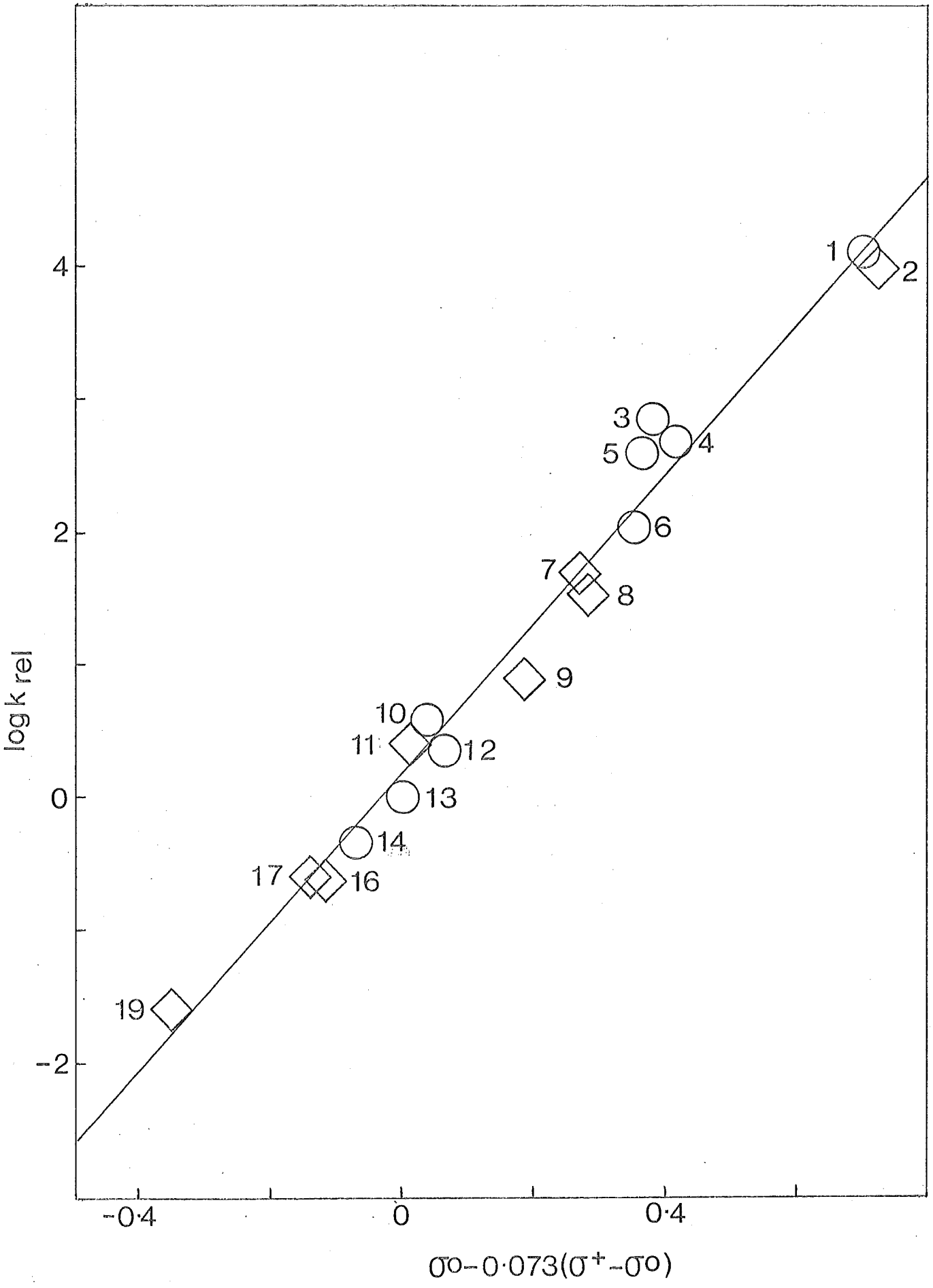


Fig. 8

Log k_{rel} vs $\sigma^0 - 0.073(\sigma^+ - \sigma^0)$ for the KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO

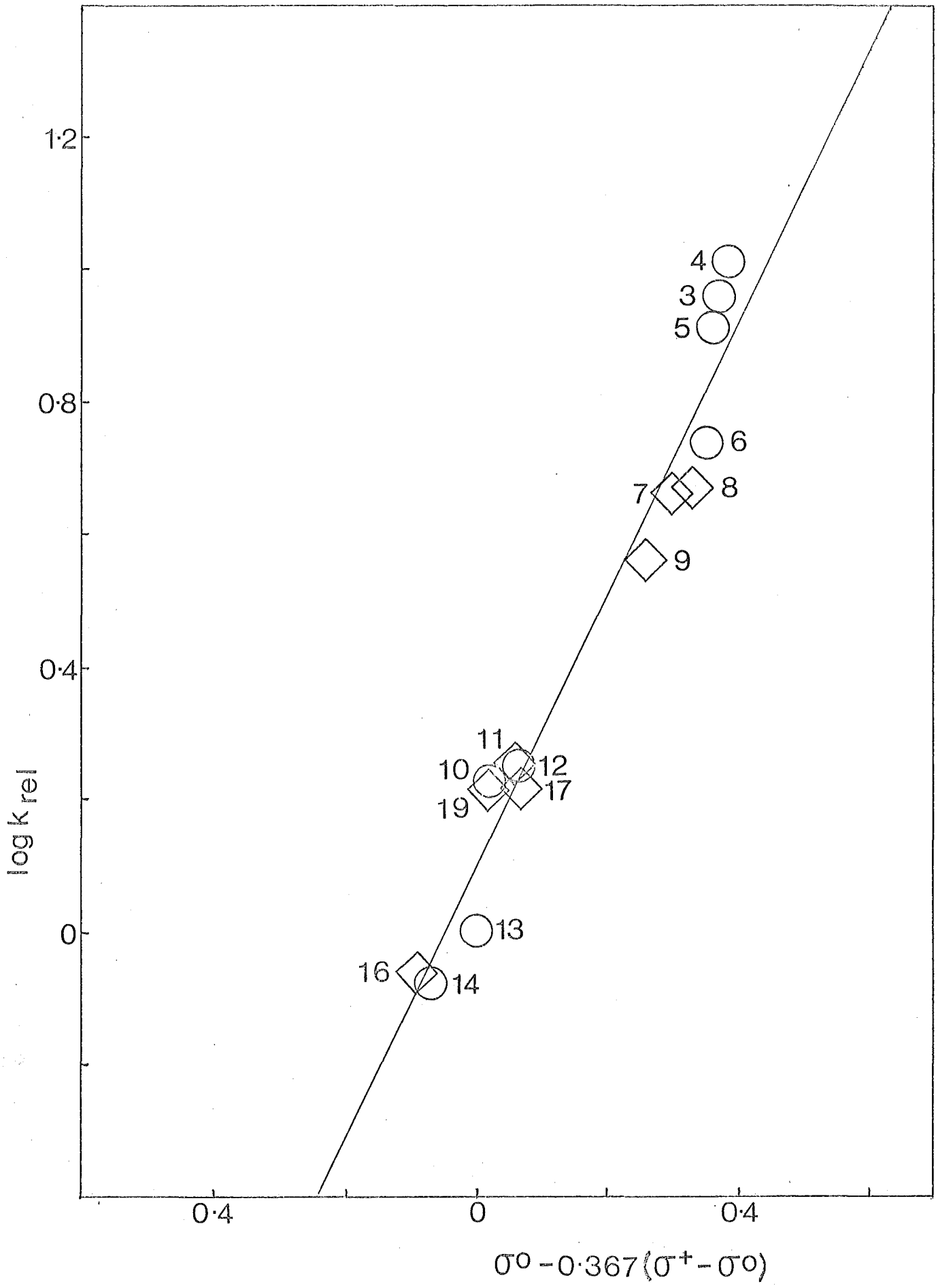


Fig. 9

Log k_{rel} vs $\sigma^0 - 0.367(\sigma^+ - \sigma^0)$ for the KOH Cleavage of $XC_6H_4SnMe_3$ in MeOH

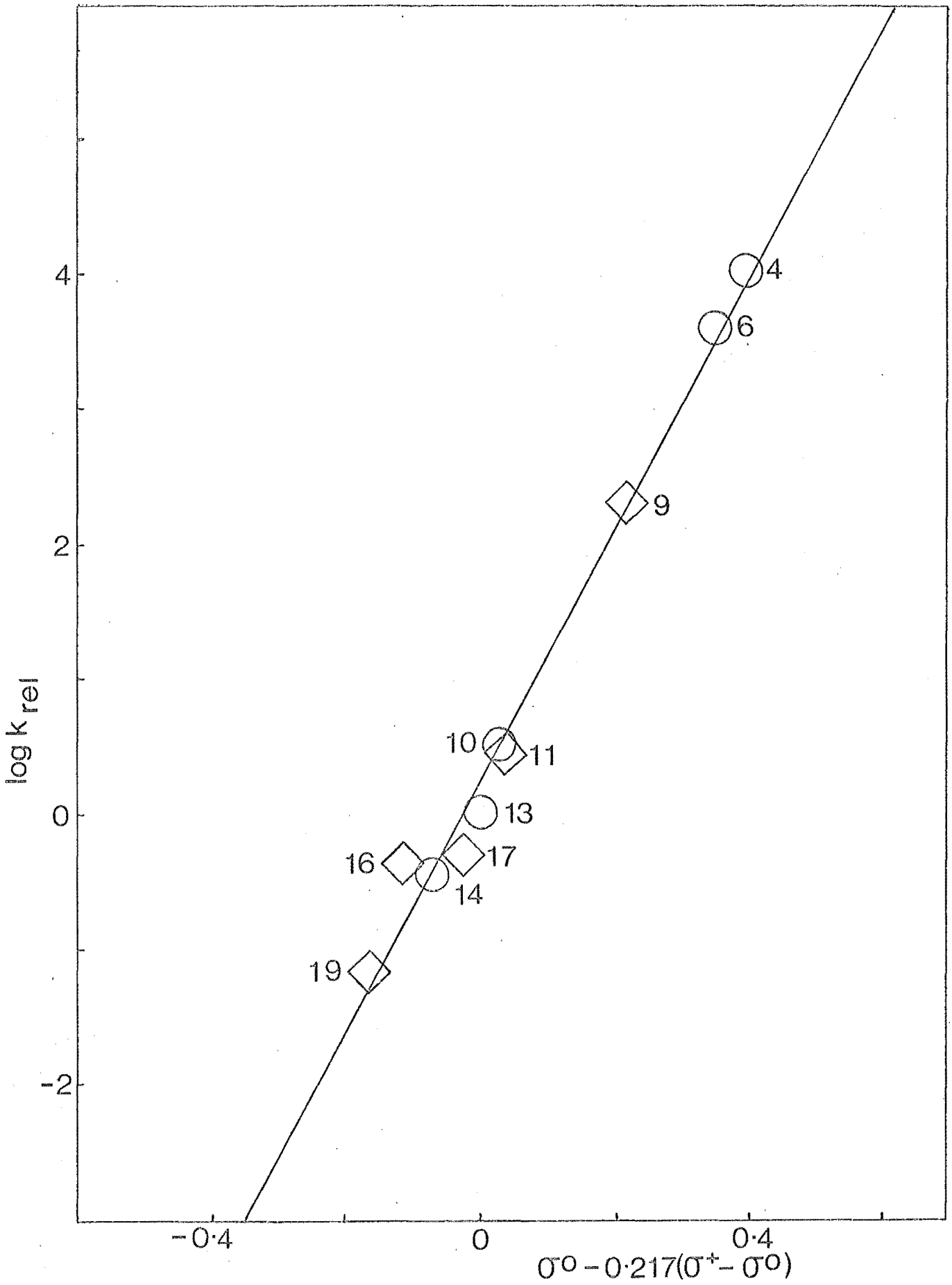


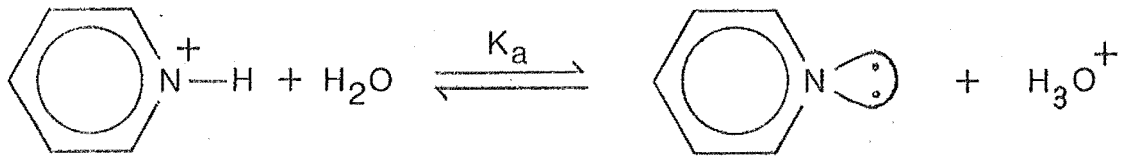
Fig. 10

Log k_{rel} vs $\sigma^0-0.217(\sigma^+-\sigma^0)$ for Base Catalysed H-Exchange in Substituted Benzenes

The σ^0 values for m-OMe and p-OMe substituents are solvent dependent, ranging from 0.13 and -0.12 in pure aqueous media to 0.06 and -0.16 respectively in non-hydroxylic or mixed aqueous organic media[65]. The latter values have been adopted for the reactions being investigated (with improved correlations as a result). The σ^0 values for para -R substituents are also solvent dependent[65]; for p-NO_2, σ^0 ranges from 0.73 (non-hydroxylic media) to 0.82 (pure aqueous and most mixed aqueous organic media). In the cleavage of aryltrimethylsilanes, the former value is adopted (as DMSO is an aprotic solvent) with a consequent improvement in correlation.

(b) The $\bar{\sigma}$ model

As mentioned earlier, there have been no substituent effect studies carried out for reactions involving purely phenyl carbanion formation as the rate determining step. However, a reaction which is isoelectronic and structurally similar is the dissociation of the pyridinium ion.



As in phenyl carbanion formation, the six-membered aromatic pyridine ring loses a proton (or some other group) to form an aromatic species with a lone pair of σ electrons in the plane of the ring. The pK_a value reflects the stability of pyridine relative to the pyridinium ion, just as the rate constant should reflect the stability of a phenyl carbanion relative to its precursor. However, since electron withdrawing

substituents decrease pK_a, ρ is negative.

The thermodynamic acid dissociation constants for meta and para substituted pyridinium ions have been measured in water at 25°C[70]. The pK_as of the meta substituted compounds correlate well with σ^0 even when constrained through the pK_a of the unsubstituted compound.

$$pK_a = -6.02\sigma^0 + 5.21 \quad (f = 0.069).$$

Both +R and -R para substituents lie above the line, but by extrapolating the pK_a values for all substituents onto this best-fit line, a set of substituent constants $\bar{\sigma}$ can be generated (Fig. 11). Table 23 gives pK_a, $\bar{\sigma}$ and comparable σ^0 values for meta and para substituents.

Table 23

σ^0 and $\bar{\sigma}$ Values for Substituents

Sub.	pK_a	$\bar{\sigma}$	σ^0	Sub.	pK_a	$\bar{\sigma}$	σ^0
m-NO_2	1.18	0.67	0.70	p-NO_2	1.39	0.63	0.82
m-CN	1.35	0.64	0.62	p-CN	1.86	0.55	0.69
m-Br	2.85	0.39	0.38	p-Br	3.75	0.24	0.26
m-Cl	2.81	0.40	0.37	p-Cl	3.83	0.23	0.27
m-F	2.97	0.37	0.35				
m-Ph	4.80	0.07	0.04	p-Ph	5.35	-0.03	0.00
m-OMe	4.78	0.07	0.13	p-OMe	6.58	-0.23	-0.12
H	5.21	0.00	0.00				
m-Me	5.67	-0.08	-0.07	p-Me	6.03	-0.14	-0.15
				p-Et	6.03	-0.14	-

In this analysis it should be noted that the pK_as for m-F and m-Ph were measured separately[71,72] from the other values

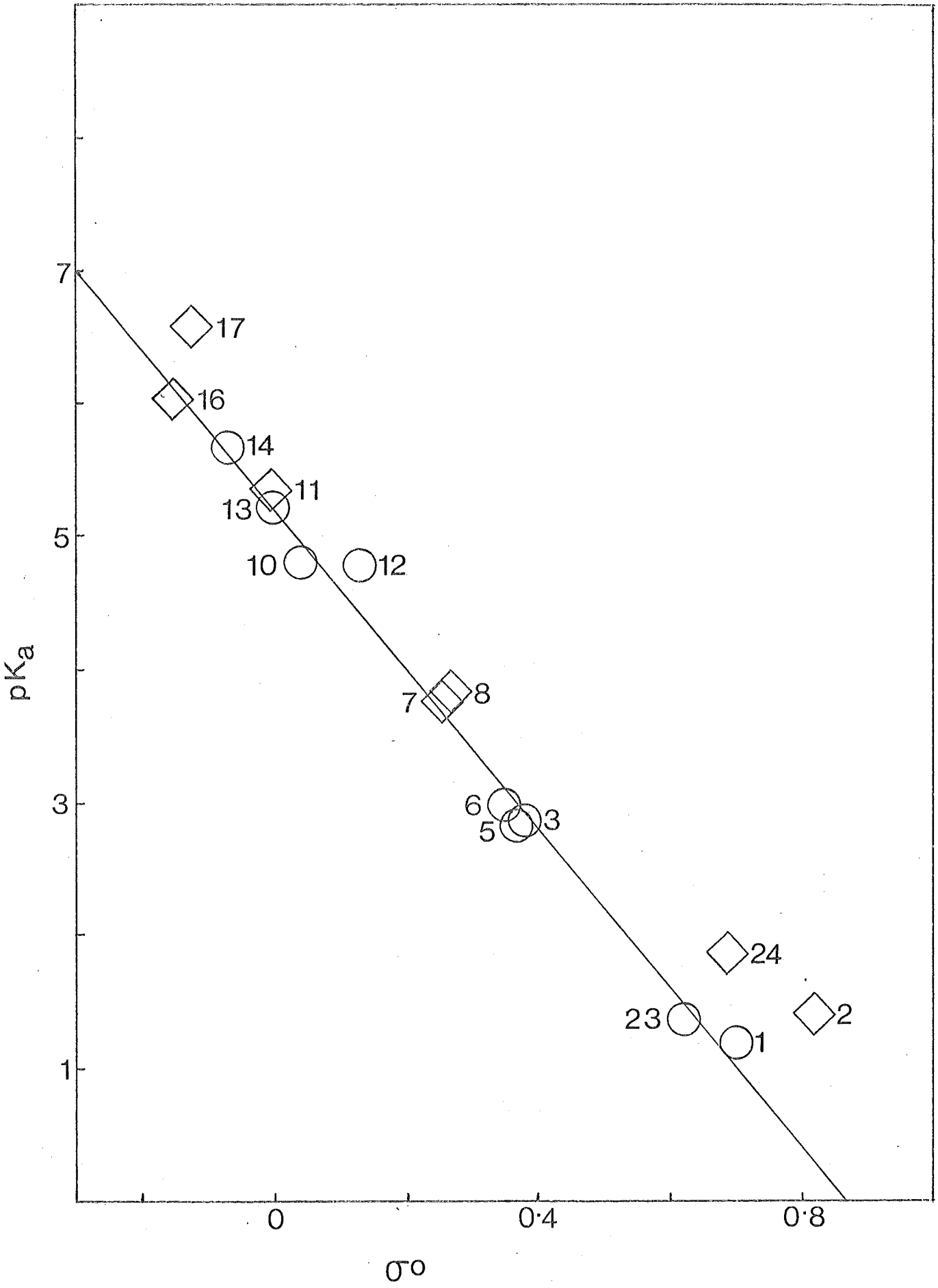


Fig. 11

pK_a vs σ^0 for the Acid Dissociation of Substituted Pyridinium Ions

so the $\bar{\sigma}$ values derived from them may be inaccurate. Although pK_as for m-NMe_2 and p-NMe_2 have been measured, protonation of the dimethylamino group occurs, making calculation of an accurate pK_a for the pyridinium ion difficult. These substituents have therefore been deleted.

For the cleavage of aryltrimethylsilanes, the meta substituents correlate well with $\bar{\sigma}$ about the line

$$\log k_{rel} = 6.15\bar{\sigma} + 0.07 \qquad (f = 0.092).$$

Only m-F and m-Br lie off the line. Para +R substituents are scattered noticeably above the line, but p-NO_2 does not deviate (Fig. 12). Good overall correlation (f = 0.095) is achieved using the expression

$$\log k_{rel} = 6.06[\bar{\sigma} - 0.176(\sigma^{+}-\bar{\sigma})] + 0.15;$$

only m-Br and m-F lie noticeably off the line. The relationship

$$\log k_{rel} = 6.06[\bar{\sigma} - 0.167(\sigma^{+}-\sigma^{0})] + 0.13$$

gives slightly better correlation (f = 0.090). Again, only m-Br and m-F lie off the line (Fig. 13).

For the cleavage of aryltrimethylstannanes in methanol, meta substituents (except m-Br, m-F) correlate well with $\bar{\sigma}$ about the line

$$\log k_{rel} = 2.09\bar{\sigma} + 0.07 \qquad (f = 0.098)$$

and para +R substituents lie noticeably above it (Fig. 14). Both meta and para substituents can be correlated by the expressions

$$\log k_{rel} = 2.04[\bar{\sigma} - 0.536(\sigma^{+}-\bar{\sigma})] + 0.08 \qquad (f = 0.109)$$

and $$\log k_{rel} = 2.06[\bar{\sigma} - 0.472(\sigma^{+}-\sigma^{0})] + 0.08 \qquad (f = 0.101).$$

In the latter, only m-F and m-Br lie off the line (Fig. 15).

For the same reaction in H_2O/DMSO, there was insufficient data for a correlation of meta substituents with $\bar{\sigma}$, but the limited range of meta and para substituents studied correlate satisfactorily using the expressions

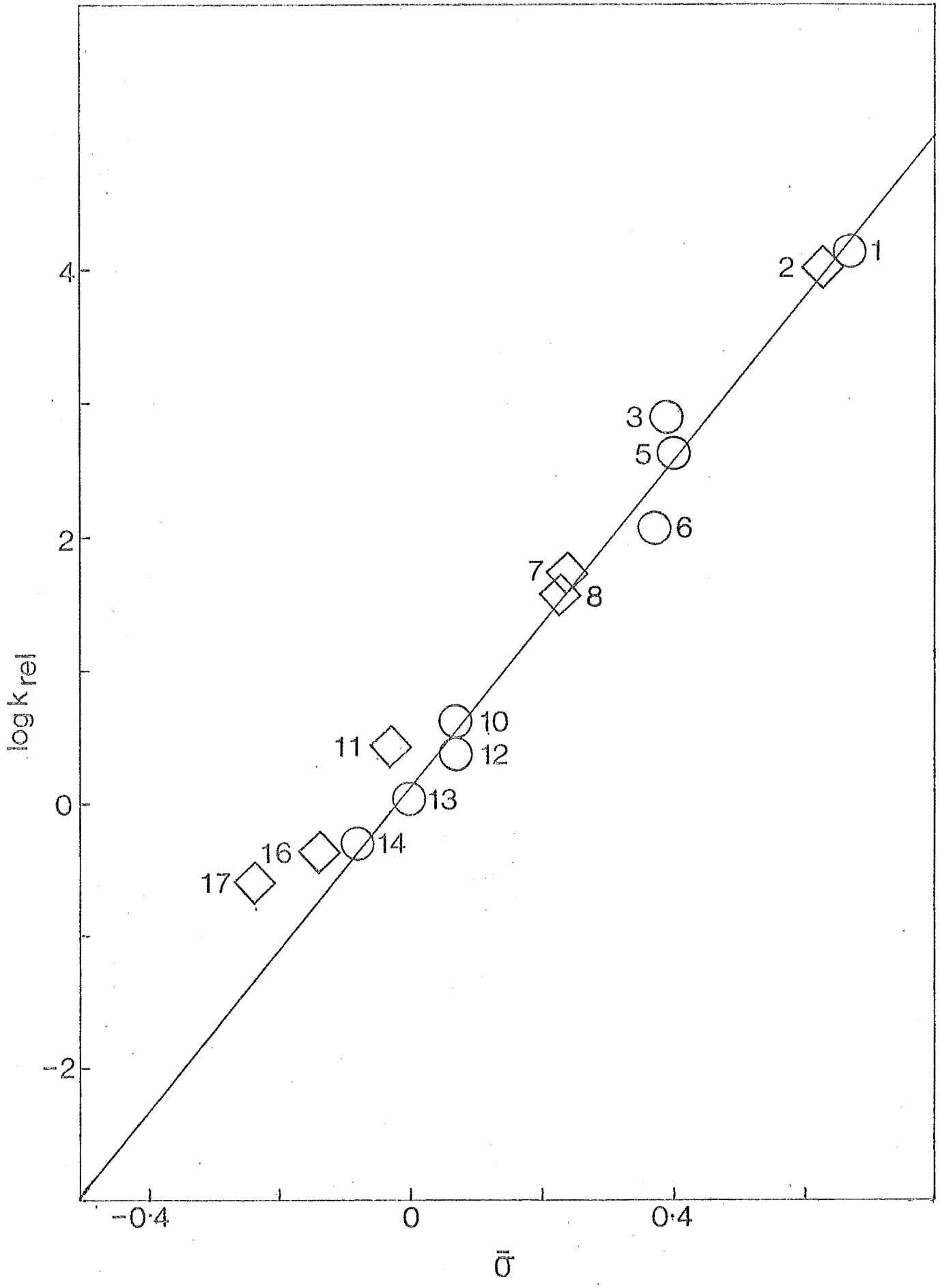


Fig. 12

Log k_{rel} vs $\bar{\sigma}$ for the KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO.

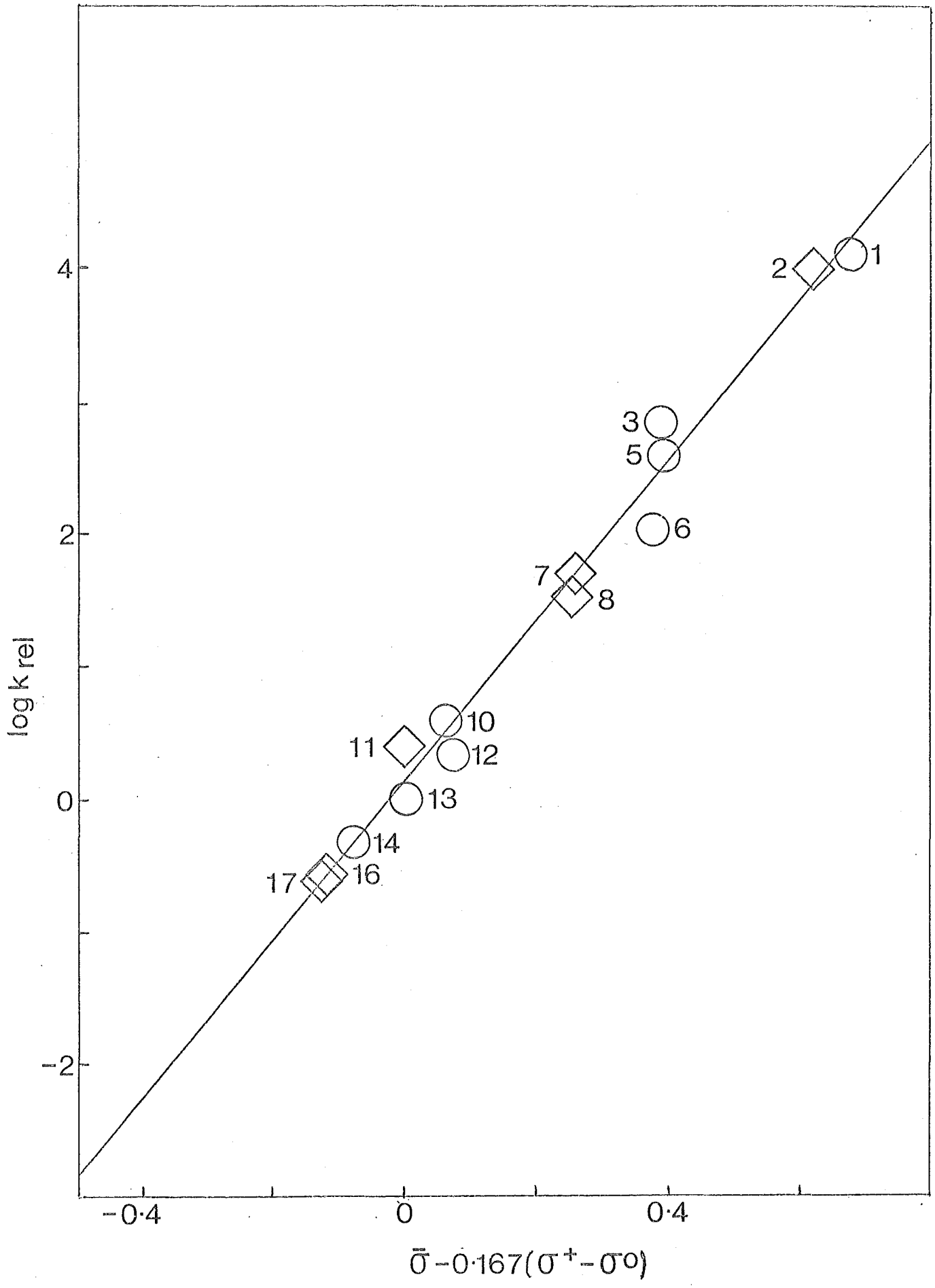


Fig. 13

Log k_{rel} vs $\bar{\sigma} - 0.167(\sigma^{+}-\sigma^{0})$ for the KOH Cleavage of $XC_6H_4SiMe_3$ in 10% v/v H_2O/DMSO

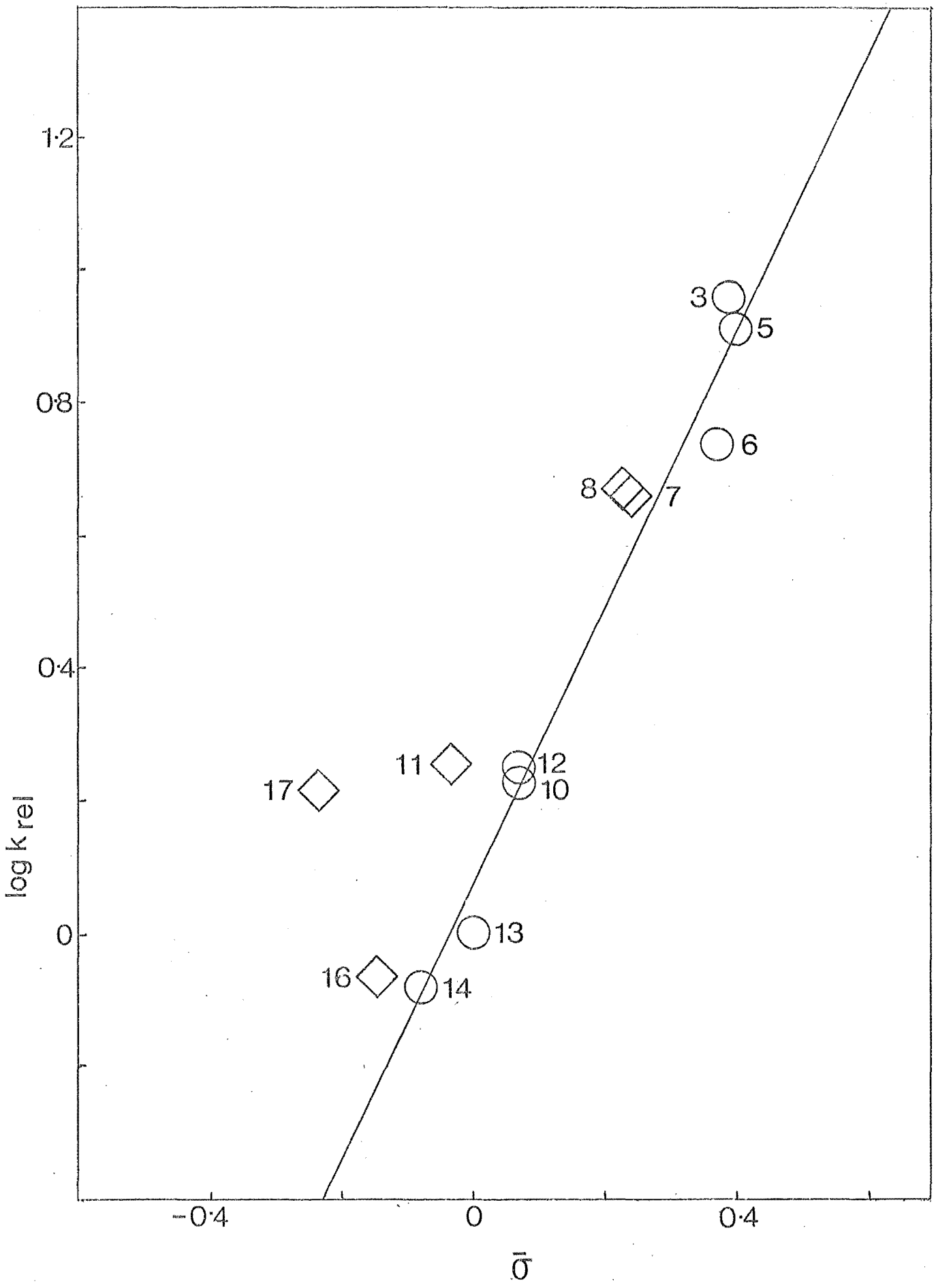


Fig. 14

Log k_{rel} vs $\bar{\sigma}$ for the KOH Cleavage of $XC_6H_4SnMe_3$ in MeOH

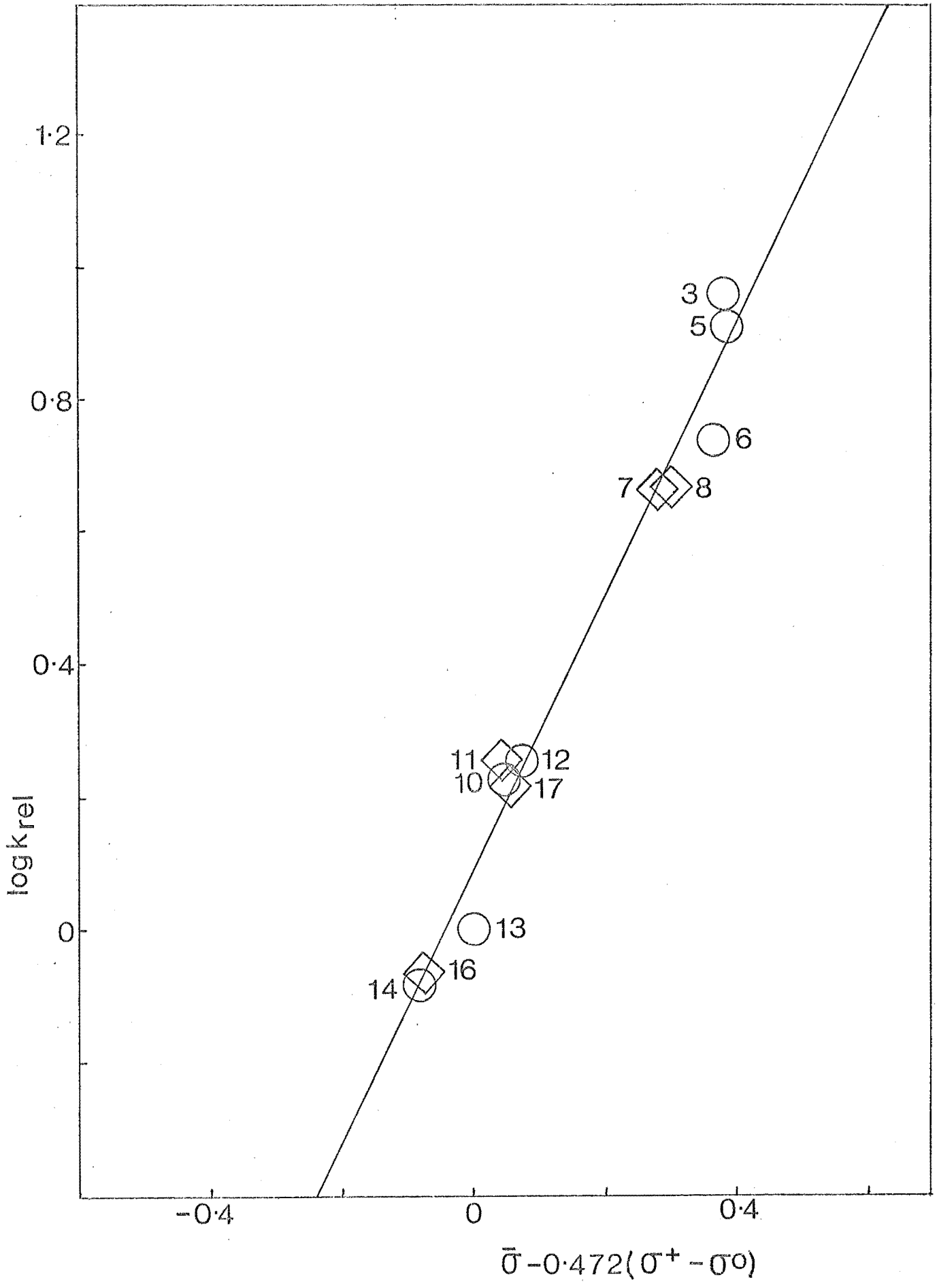


Fig. 15

Log k_{rel} vs $\bar{\sigma} - 0.472(\sigma^{+}-\sigma^{0})$ for the KOH Cleavage of $XC_6H_4SnMe_3$ in MeOH

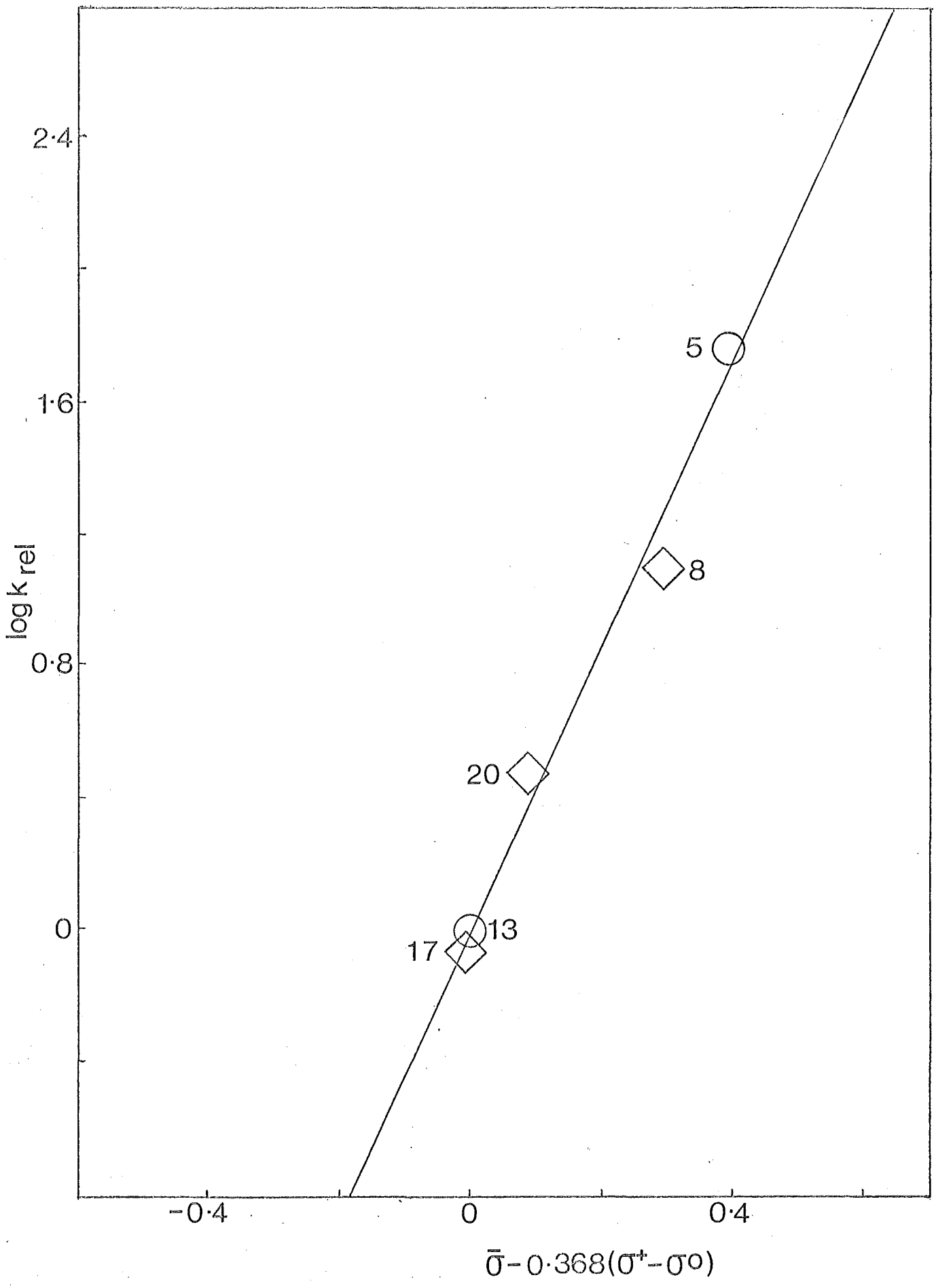


Fig. 16

Log k_{rel} vs $\bar{\sigma} - 0.368(\sigma^{+}-\sigma^{0})$ for KOH Cleavage of $XC_6H_4SnMe_3$ in 1:6 v/v H_2O/DMSO

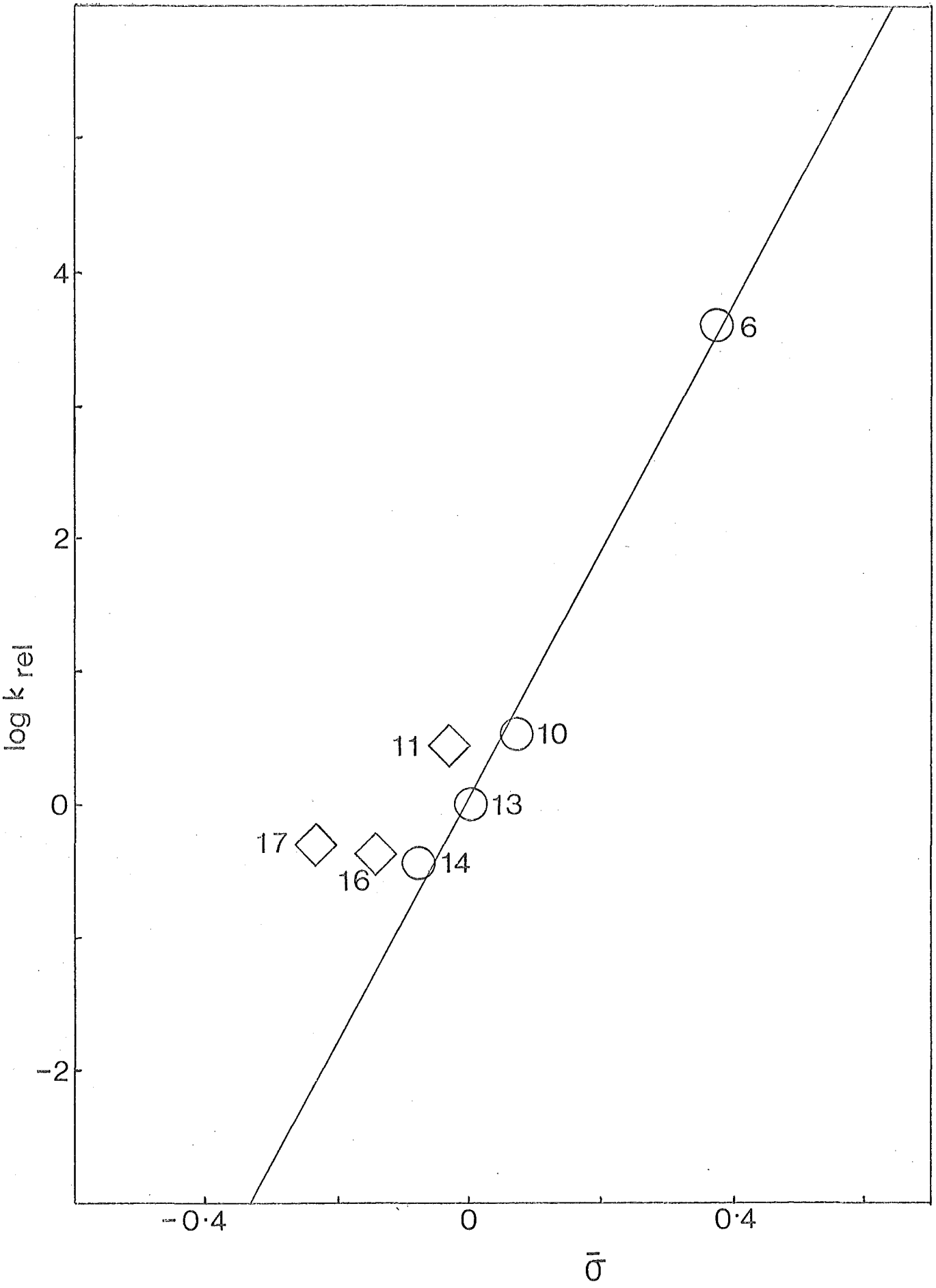


Fig. 17

Log k_{rel} vs $\bar{\sigma}$ for Base Catalysed H-Exchange in Substituted Benzenes

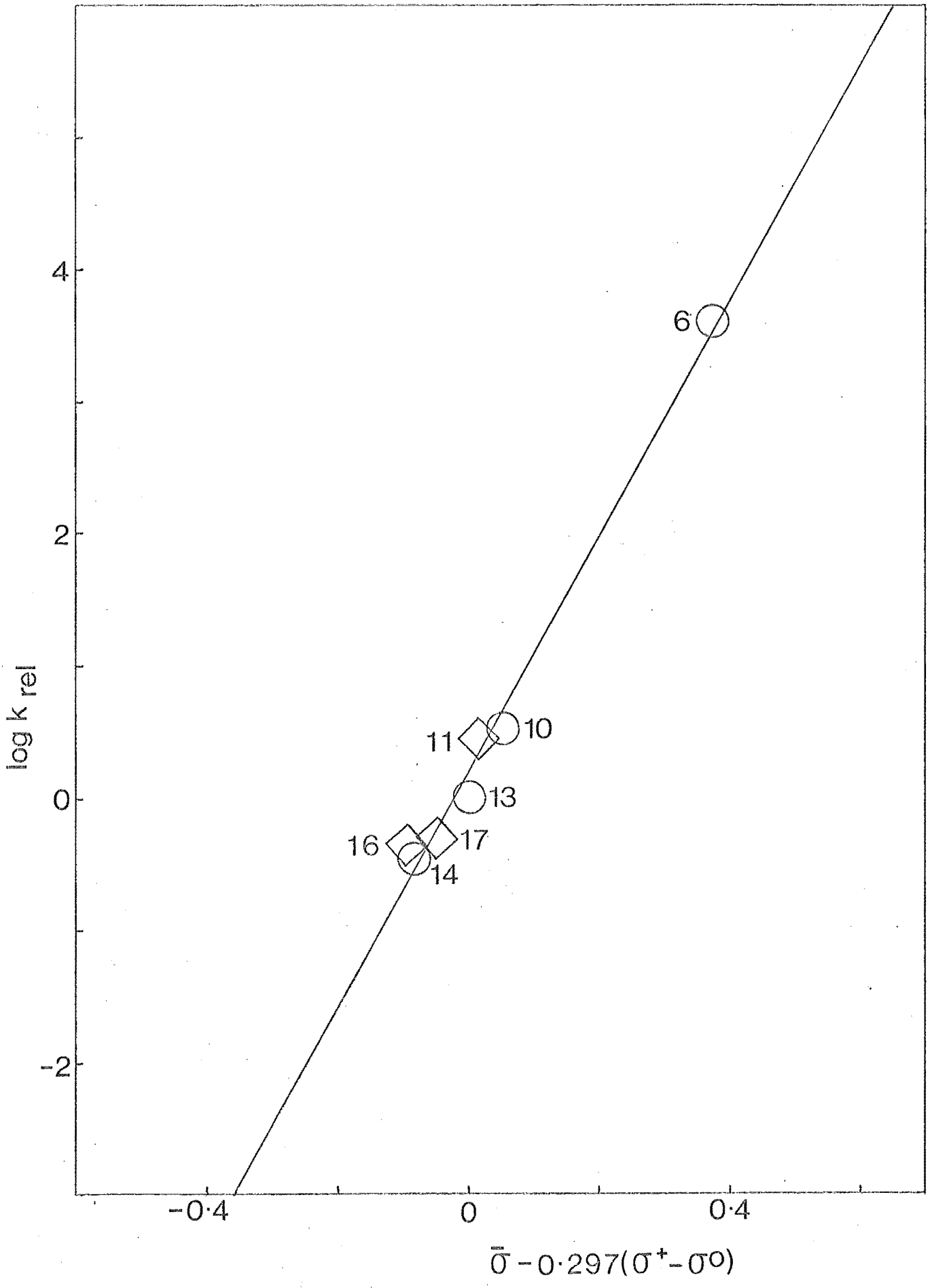


Fig. 18

Log k_{rel} vs $\bar{\sigma} - 0.297(\sigma^{+}-\sigma^{0})$ for Base Catalysed H-Exchange in Substituted Benzenes

$$\log k_{rel} = 4.33[\bar{\sigma} - 0.432(\sigma^{+}-\bar{\sigma})] + 0.02 \quad (f = 0.086)$$

and $\log k_{rel} = 4.34[\bar{\sigma} - 0.368(\sigma^{+}-\sigma^{0})] - 0.01 \quad (f = 0.093)$

(see Fig. 16).

For base catalysed H-exchange in benzene, the limited range of meta substituents correlate well (f = 0.089) with $\bar{\sigma}$ about the line

$$\log k_{rel} = 9.27\bar{\sigma} + 0.09 \text{ (Fig. 17)}.$$

Both meta and para substituents can be correlated by the expressions

$$\log k_{rel} = 8.85[\bar{\sigma} - 0.338(\sigma^{+}-\bar{\sigma})] + 0.19 \quad (f = 0.104)$$

and $\log k_{rel} = 8.93[\bar{\sigma} - 0.297(\sigma^{+}-\sigma^{0})] + 0.21 \quad (f = 0.108)$

(see Fig. 18).

Regardless of whether σ^{0} or $\bar{\sigma}$ is the better model for correlating substituent effects on a carbanion, the degree of precision achieved in the Yukawa-Tsuno relationships derived for the three reactions is strong evidence that the rate determining step is indeed carbanion formation involving electrophilic assistance by solvent. Using the $\bar{\sigma}$ set of relationships, a comparison of r values suggests that electrophilic assistance is less important in the cleavage of aryltrimethylsilanes (r = -0.167) than in the cleavage of aryltrimethylstannanes in H_2O/DMSO (r = -0.368). This may explain the greater sensitivity of the aryltrimethylsilanes to substituent changes (ρ = 6.06 for the former reaction, ρ = 4.34 for the latter). The extent of electrophilic assistance in the rate determining step appears to be solvent dependent; greater assistance is evident in the cleavage of aryltrimethylstannanes in methanol (r = -0.472) than in H_2O/DMSO (r = -0.368). This might be expected since strong hydrogen bonding occurs between H_2O and DMSO so that protons able to provide electrophilic assistance are not as readily available as in methanol.

Greater electrophilic assistance may also contribute to the lower sensitivity of the reaction in methanol ($\rho = 2.06$) than in H_2O/DMSO ($\rho = 4.34$), although the dominant factor is undoubtedly greater solvation of the transition state in H_2O/DMSO which would make rates more sensitive to substituent changes. Such solvent effects cannot be used to explain the high sensitivity to substituents in base-catalysed H-exchange ($\rho = 8.93$). One explanation might be that a greater degree of bond breaking occurs in the transition state than in aryltrimethylsilane or -stannane compounds, where bond breaking occurs more readily[68].

These conclusions were also arrived at in a previous analysis[66] based on the relationship

$$\log k_{rel} = \rho(\sigma + r\Delta^-) \qquad (14)$$

where Δ^- values are resonance parameters based on the deviations of *para* +R substituents from the best fit line through the *meta* points in the cleavage of aryltrimethylstannanes in methanol. This approach has not been adopted in this discussion; σ^0 has been used in preference to σ, and much better correlations were obtained using the Yukawa-Tsuno relationships already discussed. As a comparison, best fit expressions involving similar ranges of *para* substituents are

$$\log k_{rel} = 5.83(\sigma + 0.568\Delta^-) + 0.11 \quad (f = 0.213)$$

$$\log k_{rel} = 5.32[\sigma^0 - 0.085(\sigma^+ - \sigma^0)] + 0.10 \quad (f = 0.083)$$

The precision of Δ^- values is doubtful and their use in correlating rate constants for the cleavage of aryltrimethylsilanes and base catalysed H-exchange indicates only that the

same factors are significant in the rate determining step of all three reactions.

The consistent deviation of m-Br in correlations involving the aryltrimethylsilane series is difficult to explain. It does not appear to arise from experimental errors, as the same substituent deviates in the cleavage of aryltrimethylstannanes. It has been shown that the inductive effects of substituents are markedly altered in DMSO[73]. For example the acidities of 4-substituted bicyclo [2,2,2] octane-1-carboxylic acids measured in DMSO or 10% v/v H_2O/DMSO correlate poorly with the acidities measured in methanol or ethanol (and -Br is one of the more noticeable deviations). However, in the cleavage of aryltrimethylstannanes in methanol, m-Br still deviates. The m-F substituent also deviates in correlations based on the $\bar{\sigma}$ scale, but this could be attributed to inaccuracy in the $\bar{\sigma}$ value, as the pK_a value of the 3-fluoropyridinium ion was measured separately from the remaining substituents.

Table 24

Comparison of Correlations based on $\bar{\sigma}$ and σ^0

Reaction	Sub.	Best fit line	f	Best fit line	f
$XC_6H_4SiMe_3$ (H_2O/DMSO)	m	$6.15\bar{\sigma} + 0.07$	0.092	$6.08\sigma^0 + 0.12$	0.100
	m,p	$6.06(\bar{\sigma}-0.167(\sigma^+-\sigma^0))+0.13$	0.090	$5.62(\sigma^0-0.073(\sigma^+-\sigma^0))+0.18$	0.115
$XC_6H_4SnMe_3$ (MeOH)	m	$2.09\bar{\sigma} + 0.06$	0.098	$2.15\sigma^0 + 0.09$	0.095
	m,p	$2.06(\bar{\sigma}-0.472(\sigma^+-\sigma^0))+0.08$	0.101	$2.05(\sigma^0-0.367(\sigma^+-\sigma^0))+0.10$	0.149
$XC_6H_4SnMe_3$ (H_2O/DMSO)	m	-	-	$4.74\sigma^0 + 0.001$	0.005
	m,p	$4.34(\bar{\sigma}-0.368(\sigma^+-\sigma^0))-0.01$	0.093	$4.39(\sigma^0-0.187(\sigma^+-\sigma^0))+0.03$	0.151
base catalysed H-exchange (NH_3)	m	$9.27\bar{\sigma} + 0.08$	0.089	$9.48\sigma^0 + 0.13$	0.045
	m,p	$8.93(\bar{\sigma}-0.297(\sigma^+-\sigma^0))+0.21$	0.108	$9.23(\sigma^0-0.217(\sigma^+-\sigma^0))+0.26$	0.108

(c) Relative merits of the σ^0 and $\bar{\sigma}$ models

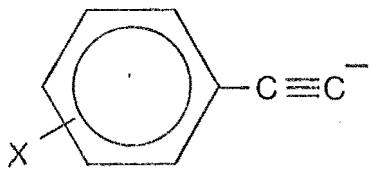
As Table 24 shows, use of $\bar{\sigma}$ gives better overall correlations than σ^0, and the correlations themselves are 'good' by the criteria discussed ($f \leqslant 0.1$). The meta substituents correlate equally well with σ^0 and $\bar{\sigma}$ as might be expected (since meta substituent constants differ very little between scales) so that the better overall correlations with $\bar{\sigma}$ arise largely from use of $\bar{\sigma}$ values for para substituents.

As mentioned, two assumptions are inherent in the σ^0 scale:

(i) direct resonance between substituent and reaction site is absent;

(ii) there is a similar balance between inductive and resonance effects between substituent and ring in both ground state and transition state.

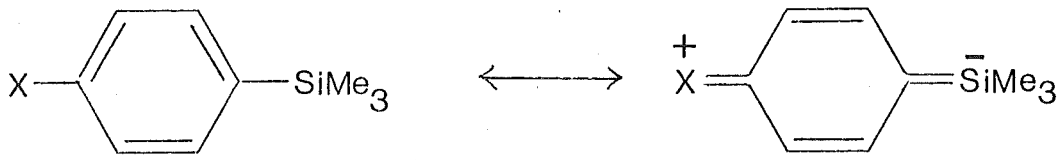
A reaction in which these conditions appear to be satisfied is the cleavage by base of substituted phenylethynylgermanes[15]. In this system, the negative charge developed in the stable carbanion is insulated from the ring.



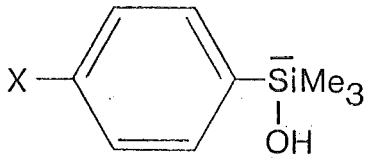
Using the published data, the meta substituents correlate well ($f = 0.069$) with σ^0, and all substituents can be successfully correlated using the expression

$$\log k_{rel} = 1.43[\sigma^0 + 0.158(\sigma^+ - \sigma^0)] + 0.02 \quad (f = 0.091).$$

In the reactions studied here, neither condition is satisfied. Although no direct conjugation can occur between substituents and the lone pair of the negative charge, the $-SiMe_3$ and $-SnMe_3$ groups are known to be moderately electron withdrawing so that ground state stabilization of the type below may occur.

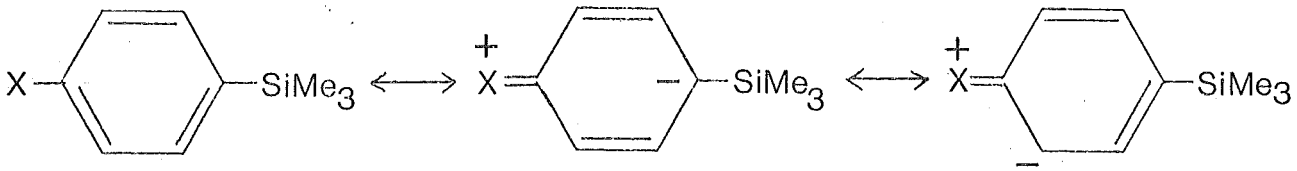


However, since the precursor in the rate determining step is more likely to be a species such as



such stabilization may be negligible, as the attraction of the vacant silicon d orbitals for π electrons is partly satisfied by hydroxide ion attack.

Secondly, if carbanion development occurs, the presence of a lone pair would disturb the normal resonance interaction of a substituent with the ring. Substituents capable of conjugation with the ring localize charge at the ortho and para positions, so that para substituents will tend to localize charge at the reaction site.



If the transition state involves carbanion formation, electron repulsion would rule out structures such as II (Fig. 19).

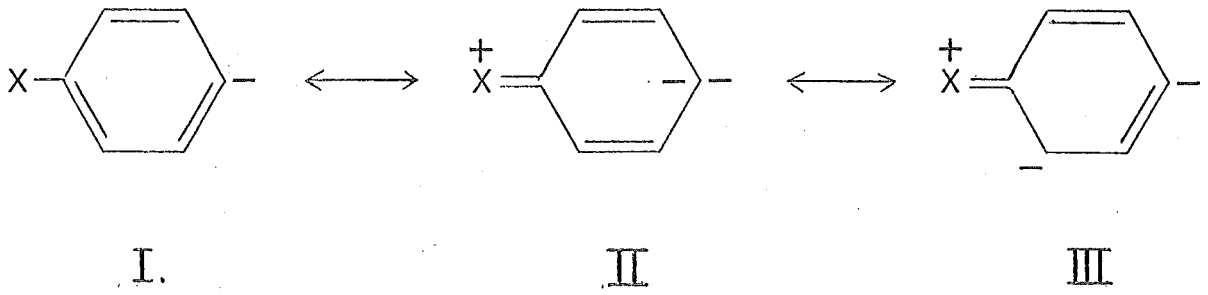
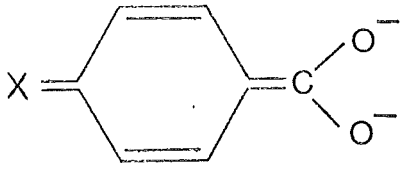
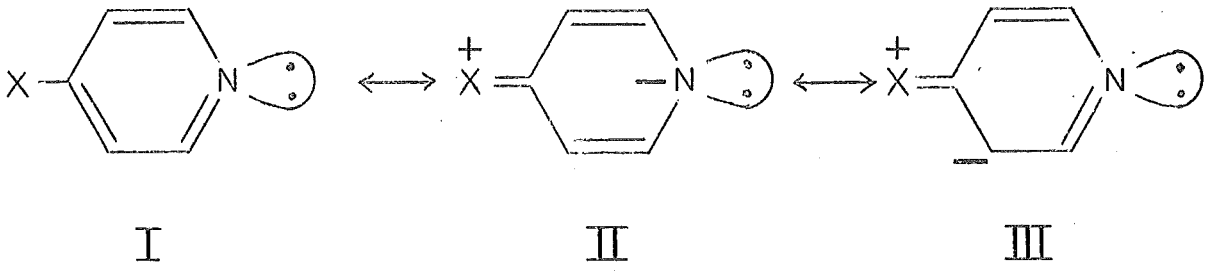


Fig. 19

The resulting destabilization of the transition state would increase the activation energy to give a rate constant lower than expected from the σ^0 value of the substituent. Such an effect has been suggested to explain the discrepancy between σ and σ^0 values for para +R substituents, as similar electron repulsions occur in one of the structures contributing to the carboxylate anion (see earlier discussion).



Similarly, in the dissociation of pyridinium ions, the pK_a values of para +R substituted compounds are higher than expected, suggesting that the pyridine form lacks the resonance stabilization of the pyridinium ion. Because of the similarities between pyridine and a phenyl carbanion, electron repulsion would rule out the pyridine form II (fig. 19a) and explain the high pK_as (and hence low $\bar{\sigma}$ values) for +R substituents.



I II III

Fig. 19a

Although the $\bar{\sigma}$ scale therefore appears to be a better model than σ^0 for the effects of +R substituents on a phenyl carbanion, the low $\bar{\sigma}$ values for -R substituents are not readily rationalized. The high pK_a values for substituents such as p-NO_2 and p-CN give rise to $\bar{\sigma}$ values closer to σ_I than σ^0. The explanation given is that the normal resonance between substituent and ring is inhibited due to opposing resonance withdrawal by the electronegative nitrogen in both pyridine and the pyridinium ion. Such an argument is invalid if the reaction is to be taken as a model for carbanion formation.

Until an explanation is put forward which is consistent with both pyridine and a carbanion, the $\bar{\sigma}$ model is unsatisfactory for -R substituents and the apparent correlation of p-NO_2 in the cleavage of aryltrimethylsilanes may be merely fortuitous.

(iv) The Dual Parameter Relationship

In a recent paper[64], Ehrenson, Brownlee and Taft presented a comprehensive statistical analysis showing that the overall effect of a substituent is a blend of polar and resonance effects, and can be expressed as

$$\log k_{rel} = \rho_I\sigma_I + \rho_R\sigma_R^x)$$

$$= \rho_I(\sigma_I + \lambda\sigma_R^x) \qquad (15)$$

where $\lambda = \rho_R/\rho_I$, and the mixing coefficients ρ_I and ρ_R depend on the position of the substituent, the nature of the reaction and the reaction conditions. A single scale of polar effects, σ_I, is postulated, but four distinct scales of resonance effects ($\sigma_R^x = \sigma_R$, σ_R^0, σ_R^+, σ_R^-) are suggested to cater for different reaction types. These are:

(i) σ_R scale - for reactions in which the reaction site is a weak π electron acceptor (e.g. ionization of benzoic acids)

(ii) σ_R^0 scale - for reactions in which resonance interaction occurs only between substituent and ring (e.g. ionization of phenylacetic acids)

(iii) σ_R^+ scale - for reactions in which the reaction site is a strongly interacting π electron acceptor (e.g. in electrophilic aromatic substitution)

(iv) σ_R^- scale - tor reactions in which the reaction site is a strongly interacting π electron donor (e.g. ionization of anilinium ions).

As Table 25 shows, m substituents in the cleavages of both aryltrimethylsilanes and -stannanes correlate most satisfactorily using σ_R. However the correlations using σ_R^0, σ_R^+ are not significantly worse, as might be expected since the resonance component for meta substituents is small. Para substituents in neither reaction correlate satisfactorily with any of the resonance parameters. Although para substituents in the cleavage of aryltrimethylsilanes show a reasonable correlation using σ_R^0 (f = 0.115), the correlation of similar substituents with σ_R^0 in the cleavage of aryltrimethylstannanes is poor (f = 0.291). One can only conclude that the resonance effects of substituents in these reactions do not fit the usual categories represented by σ_R, σ_R^0, σ_R^+ or σ_R^-. This might be expected if the resonance effect of a substituent on the reaction is a twofold one, as the previous analysis suggests.

By contrast, the ΔpK_as of the pyridinium ions correlate much more satisfactorily, especially with σ_R^+ (f = 0.033 for meta substituents, f = 0.037 for para substituents). The λ values of 0.169, (meta series) and 0.517 (para series) are considerably lower than the values usually prevailing for reactions where conjugation occurs between +R substituents and the reaction site (λ ≈ 0.4(m) and 1.0(p)). This suggests that resonance interaction between substituent and reaction site is inhibited in the transition state, probably because forms such as

Table 25

Best Fit Dual Parameter Relationships [$\log k_{rel} = \rho_I(\sigma_I + \lambda\sigma_R^x)$]

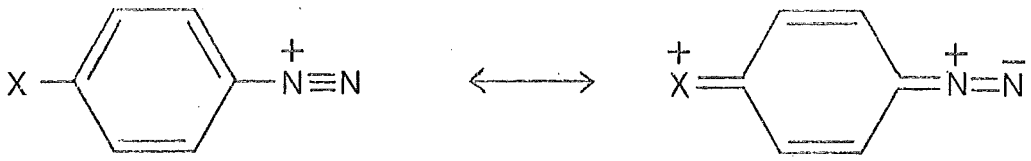
Reaction	Sub.	n	σ_R^x	ρ_I	λ	f	Sub.	n	σ_R^x	ρ_I	λ	f
$XC_6H_4SiMe_3$ in H_2O/DMSO	m	10	-	5.45	-	0.294	p	9	-	3.69	-	0.614
		10	σ_R	6.05	0.272	0.109		9	σ_R	4.99	0.563	0.147
		10	σ_R^0	6.07	0.364	0.133		9	σ_R^0	5.15	0.782	0.115
		10	σ_R^+	5.97	0.141	0.134		9	σ_R^+	4.74	0.292	0.255
		10	σ_R^-	5.67	0.301	0.176		9	σ_R^-	4.40	0.751	0.206
$XC_6H_4SnMe_3$ in MeOH	m	9	-	1.81	-	0.302	p					
		9	σ_R	2.19	0.253	0.098		9	σ_R	1.49	0.072	0.297
		9	σ_R^0	2.24	0.360	0.129		9	σ_R^0	1.52	0.132	0.291
		9	σ_R^+	2.12	0.134	0.130		9	σ_R^+	1.43	0.011	0.305
ΔpK_a for dissociation of $XC_5H_5N^+$	m	7	σ_R	-5.94	0.311	0.034	p	7	σ_R	-5.01	0.880	0.057
		7	σ_R^0	-6.00	0.437	0.096		7	σ_R^0	-5.03	1.063	0.124
		7	σ_R^+	-5.96	0.169	0.033		7	σ_R^+	-5.20	0.517	0.037
		7	σ_R^-	-5.37	0.364	0.158		7	σ_R^-	-3.75	0.968	0.281

are not favoured (for reasons already discussed). Although the rates of cleavage of <u>para</u> substituted aryltrimethylsilanes and -stannanes show poor correlation with σ_R^+, the low λ values obtained (0.292, 0.011) are informative since, if +R groups enhance electrophilic assistance yet hinder development of negative charge at the reaction site, λ should be considerably reduced (and possibly negative). Also, the value of λ is lower for aryltrimethylstannanes than -silanes, consistent with the previous conclusion that greater electrophilic assistance occurs in the former reaction.

A similar but inverted pattern of substituent effects compared with the reactions being studied, occurs in the solvolysis of substituted phenyldiazonium ions[74,75]. The rates can be correlated using the expression[64]

$$\log k_{rel} = -4.09(\sigma_I - 0.67\sigma_R^+) \quad (f = 0.081)$$

This is one of the few reactions exhibiting a negative λ value; it is thought that +R effects inhibit transition state formation (even though electron supply enhances the overall reaction), because the resonance stabilization possible in the diazo reactant is diminished in the carbonium ion-like transition state



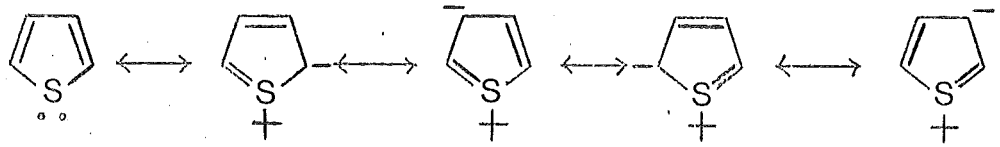
In addition, nucleophilic assistance by the solvent accompanies $C-N_2^+$ bond cleavage[76], and such assistance would be aided by resonance withdrawal from the reaction site.

KOH CLEAVAGE OF HETEROCYCLIC DERIVATIVES

The electronic effects of replacing the $-CH=CH-$ linkage in benzene by heteroatoms such as oxygen or sulphur are:

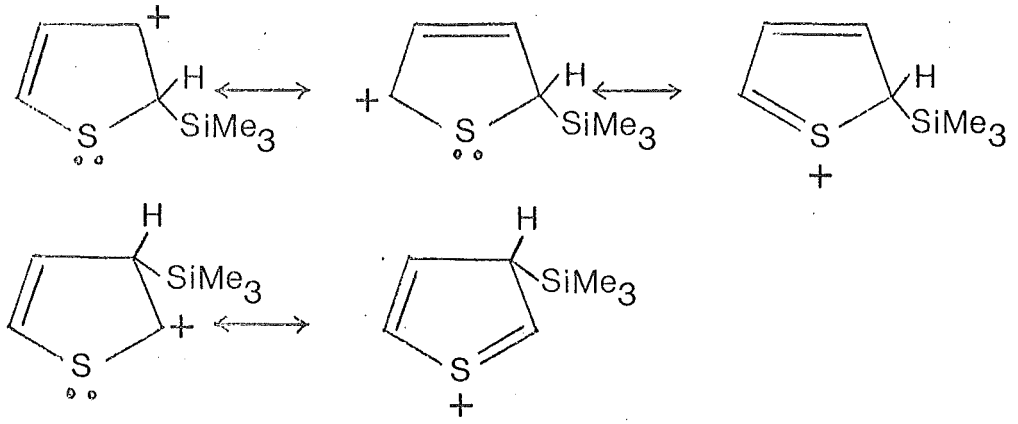
(i) inductive electron withdrawal towards oxygen or sulphur, as both are more electronegative than carbon;

(ii) conjugative electron release by oxygen or sulphur, as both atoms possess pairs of unshared electrons, e.g.



Because oxygen is more electronegative than sulphur, it is a stronger inductive withdrawer, but sulphur is a stronger lone pair donor than oxygen[77].

In electrophilic aromatic substitution, conjugative release is the dominant factor; intermediate formation is stabilized by +R effects from the heteroatom, so both furan and thiophene are more reactive than benzene. For example, the relative rates for perchloric acid cleavage of 2-furyl-, 2-thienyl- and phenyltrimethylsilane are 17,200 : 4810 : 1[78]. Although sulphur is a stronger +R group than oxygen, 2-furyltrimethylsilane reacts more rapidly because lower localization energy is involved in forming the intermediate[77] (furan is less aromatic than thiophene or benzene). The fact that 2-thienyltrimethylsilane cleaves 43 times faster than 3-thienyltrimethylsilane[79] is attributable to the greater stabilization possible in the intermediate. While three canonical forms can be written for the intermediate in 2-thienyltrimethylsilane cleavage, only two can be written for the intermediate from the three substituted compound.



In alkali cleavage of these compounds, a similar order of reactivity is evident. In 33% v/v H_2O/DMSO, 2-thienyltrimethylsilane cleaves 1330 times faster than 3-thienyltrimethylsilane, and in 50% v/v MeOH/DMSO, 2-furyltrimethyl-

silane cleaves 1.3 times faster than 2-thienyltrimethylsilane. All three species are considerably more reactive than phenyltrimethylsilane; 2-furyl- and 2-thienyltrimethylsilane are at least 20 times more reactive than trimethyl(m-nitrophenyl)-silane, and 3-thienyltrimethylsilane is comparable in reactivity to (m-fluorophenyl)trimethylsilane (see Table 7).

These results can be explained in terms of the mechanism suggested for alkali cleavage. The high overall reactivity of these compounds is understandable since electron withdrawal by sulphur or oxygen would enhance the development of negative charge on the aromatic ring. Simple inductive effects would also explain why 2-thienyltrimethylsilane is more reactive than 3-thienyltrimethylsilane, and 2-furyltrimethylsilane more reactive than 2-thienyltrimethylsilane. However, the impact of electrophilic assistance must also be considered. Electrophilic attack occurs preferentially at the 2 position, further enhancing the relative reactivity of the 2-substituted compound compared with the 3-substituted compound. Because sulphur is a better lone pair donor than oxygen, electrophilic assistance should be more effective in 2-thienyl- than 2-furyltrimethylsilane. This may explain why 2-furyltrimethylsilane is only slightly more reactive than 2-thienyltrimethylsilane.

Metallation of heterocyclic aromatic compounds is believed to operate by a mechanism similar to that proposed for alkali cleavage, so it is relevant to note that metallation of thiophene by n-BuLi in DMSO occurs 2.5×10^5 times more rapidly at the 2 position than at the 3 position[80].

THE ACIDITY FUNCTION H_-

The basicity of media such as aqueous alkaline DMSO is measured by the acidity function H_-. If an indicator AH is placed in such a medium, the equilibrium set up when the medium abstracts a proton is

$$AH + OH^- \rightleftharpoons A^- + H_2O$$

or $$AH + OH^-(H_2O)_n \rightleftharpoons A^- + (n+1)H_2O$$

if hydroxide ion is highly solvated. The equilibrium constant K_{AH} of the indicator is based on the equilibrium

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_{AH} = \frac{a_{A^-} \cdot a_{H_3O^+}}{a_{AH}} \quad \text{where a = activity} \qquad (16)$$

$$\text{i.e. } K_{AH} = \frac{f_{A^-}[A^-]}{f_{AH}[AH]} \cdot a_{H_3O^+}$$

where f = activity coefficient.

Hence

$$\log_{10}K_{AH} = \log_{10}\frac{[A^-]}{[AH]} + \log_{10} a_{H_3O^+} \cdot \frac{f_{A^-}}{f_{AH}}$$

and rearranging:

$$-\log_{10}a_{H_3O^+} \cdot \frac{f_{A^-}}{f_{AH}} = \log_{10}\frac{[A^-]}{[AH]} - \log_{10}K_{AH} \qquad (17)$$

in very dilute solutions, $f \to 1$, and $a_{H_3O^+} \to [H_3O^+]$

$$\text{i.e. } -\log_{10}[H_3O^+] = pH = \log_{10}\frac{[A^-]}{[AH]} + pK_{AH}. \qquad (18)$$

In dilute solutions, pH is the accepted measure of the ability of the medium to abstract a proton; in concentrated solutions the comparable measure is H_-, where

$$H_- = -\log_{10} \frac{a_{H_3O^+} f_{A^-}}{f_{AH}} \tag{19}$$

since

$$H_- = -\log_{10} \frac{a_{H_3O^+} f_{A^-}}{f_{AH}} = \log_{10} \frac{[A^-]}{[AH]} + pK_{AH}.$$

The H_- value of a solvent system may be determined using indicators of known K_{AH} and measuring the extent of their ionization.

If nucleophilic activity in a reaction (as measured by the pseudo first order rate constant k_{obs}) is primarily dependent on basicity, it can be shown that a linear relationship should exist between log k_{obs}, and H_-, or more precisely, between log k_{obs} and $H_- + \log_{10} a_{H_2O}$[81].

Where a proton is removed from the substrate SH in the rate determining step

$$SH + OH^- \xrightarrow[\text{slow}]{} S^- + H_2O$$

$$S^- \xrightarrow[\text{fast}]{} \text{products},$$

then by the absolute rate theory

$$-\frac{d[SH]}{dt} = k[SH]a_{OH^-} \frac{f_{SH}}{f_{\ddagger}} \tag{20}$$

where f_{SH} and $f_{\ddagger}$ are activity coefficients for the reactant and transition state respectively.

By definition, $H_- = -\log_{10} a_{H_3O^+} \cdot \frac{f_{A^-}}{f_{AH}}$

$$\text{or} \quad h_- = a_{H_3O^+} \cdot \frac{f_{A^-}}{f_{AH}} \qquad \text{where} \quad H_- = -\log_{10} h_-$$

$$K_w = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}} \tag{21}$$

substituting

$$h_- = \frac{K_w a_{H_2O} \, f_{A^-}}{a_{OH^-} \, f_{AH}} \tag{22}$$

If the ground and transition states of the reaction being studied bear a similar relationship to that between the indicator used to set up the H_- scale, and its anion,

$$\frac{f_{A^-}}{f_{AH}} \approx \frac{f_{\neq}}{f_{SH}}$$

$$\text{i.e.} \quad h_- = \frac{K_w \, a_{H_2O} \, f_{\neq}}{a_{OH^-} \, f_{SH}}$$

substituting for $\frac{f_{\neq}}{f_{SH}}$ in equation (20)

$$-\frac{d[SH]}{dt} = \frac{kK_w a_{H_2O}}{h_-} [SH] \tag{23}$$

$$\text{but} \quad -\frac{d[SH]}{dt} = k_{obs} [SH]$$

since the reaction is first order in substrate,

$$\text{i.e.} \quad k_{obs} = \frac{kK_w \, a_{H_2O}}{h_-} \tag{24}$$

$$\log k_{obs} = -\log h_- + \log a_{H_2O} + \log K_w + \log k$$

$$= H_- + \log a_{H_2O} - pK_w + \text{constant.} \tag{25}$$

Assuming pK_w to be constant, there should be a linear relationship between the logarithms of the pseudo first order rate constants and H_- + log a_{H_2O}, with unit slope.

To see if such a relationship exists in the reaction under investigation, the rates of cleavage of $ArSiMe_3$ by 0.05M KOH were measured in media ranging from 3% v/v H_2O/DMSO to $33\frac{1}{3}$% v/v H_2O/DMSO, at 40.0°C, and the pseudo first order rate constants derived from these rate data using the ORGLS least squares program (see Table 8).

Because of the wide range of reactivity encountered, one substrate could not be used for all measurements; four substrates of varying reactivity were employed (2-thienyl-, p-nitrophenyl, m-fluorophenyl- and p-fluorophenyltrimethylsilane) and the results overlapped (see Table 26). Unfortunately rate dependence on the medium differed slightly between substrates, so to determine overall relative rate constants, the cleavage of m-$FC_6H_4SiMe_3$ in 85% v/v H_2O/DMSO was taken as the standard reaction (k_{rel} = 1.00) and overlapping of results achieved by measuring the rates for pairs of substrates in several media. By extrapolating the log-log correlation of these rate constants, it is possible to derive log k_{rel} values for other media. For example, the plot of log k_{rel}^{m-F} versus log k_{rel}^{p-F} for rates measured in 92, 94 and 95% v/v H_2O/DMSO can be extrapolated to find log k_{rel}^{m-F} in 96% and 97% v/v H_2O/DMSO. The log-log plots were all excellent straight lines, slope ≈ 1, and could be accurately extrapolated. As Table 26 shows, a 10^5 variation in reactivity was achieved by overlapping measurements. It was not convenient to measure rates in media >33% v/v H_2O/DMSO; none of the substrates was sufficiently reactive.

Table 26

H_- Values and Relative Rate Constants for Cleavage by KOH in Aqueous DMSO

mole % DMSO	$H_-^{0.011M}$	$H_-^{0.05M}$	f_{H_2O}	$H_-^{0.05M} + \log a_{H_2O}$	k_{rel} ($ArSiMe_3$)				log k_{rel} (overall)
					2-Thienyl-	$\underline{p}NO_2C_6H_4$-	$\underline{m}FC_6H_4$-	$\underline{p}FC_6H_4$-	
33.41	15.83	16.49	0.668	17.59	1.000				-2.38
42.94	16.78	17.44	0.562	18.33	8.175	1.000			-1.44
46.35	17.12	17.78	0.531	18.61	17.50	2.475			-1.11
50.09	17.57	18.23	0.490	18.97	37.77	6.519			-0.760
58.70	18.35	19.01	0.432	19.57		51.71	1.000		0.000
61.99	18.69	19.35	0.410	19.83		122.7	2.067		0.315
69.30	19.42	20.08	0.370	20.40			10.00		1.00
74.26	19.95	20.61	0.345	20.80			37.04	1.000	1.57
79.72	20.52	21.18	0.322	21.21			105.2	3.058	2.02
82.66	20.90	21.56	0.309	21.49			186.7	5.739	2.27
85.76	21.27	21.93	0.297	21.75				9.975	2.49
89.02	21.78	22.44	0.283	22.11				15.49	2.67
90.73	22.05	22.71	0.277	22.29				25.06	2.87

The H_- values shown in Table 26 were derived by interpolation of a plot of H_- versus mole percent DMSO based on the ionization of substituted anilines in 0.011M tetramethylammonium hydroxide[82]. As the rates of cleavage of $ArSiMe_3$ were measured in 0.05M KOH, the H_- values have been adjusted accordingly[83].

$$H_-^{0.05M} = H_-^{0.011M} + \log_{10} \frac{0.05}{0.011}$$

$$= H_-^{0.011M} + 0.66 \qquad (26)$$

It may be assumed that the same H_- values hold for $Me_4N^+OH^-$ as KOH; only at high concentrations (>2M) do values differ for different bases because of ion association[84].

The activity coefficients f_{H_2O}, for water in DMSO, were derived by interpolation from a plot of log f_{H_2O} versus mole fraction DMSO[85], and the activity of water a_{H_2O} calculated using the expression

$$a_{H_2O} = f_{H_2O}[H_2O] \qquad (27)$$

where $[H_2O]$ is the molar concentration of water.

There is excellent correlation (f = 0.023) even between log k_{rel} and H_- (slope 0.945) over the range 33.41 - 74.26 mole percent DMSO, corresponding to a 10^4 variation in rate (Fig. 20). Above 74.26 mole percent DMSO (92% v/v), the slope decreases. Such a correlation of log k_{rel} with H_- assumes that the activity of water does not greatly vary with changing water concentration. However, not only does $[H_2O]$ drop with increasing mole percent DMSO, but f_{H_2O} also drops markedly because of extensive DMSO-H_2O interaction. Good correlation (f = 0.026) occurs up to 82.66 mole percent DMSO (95% v/v)

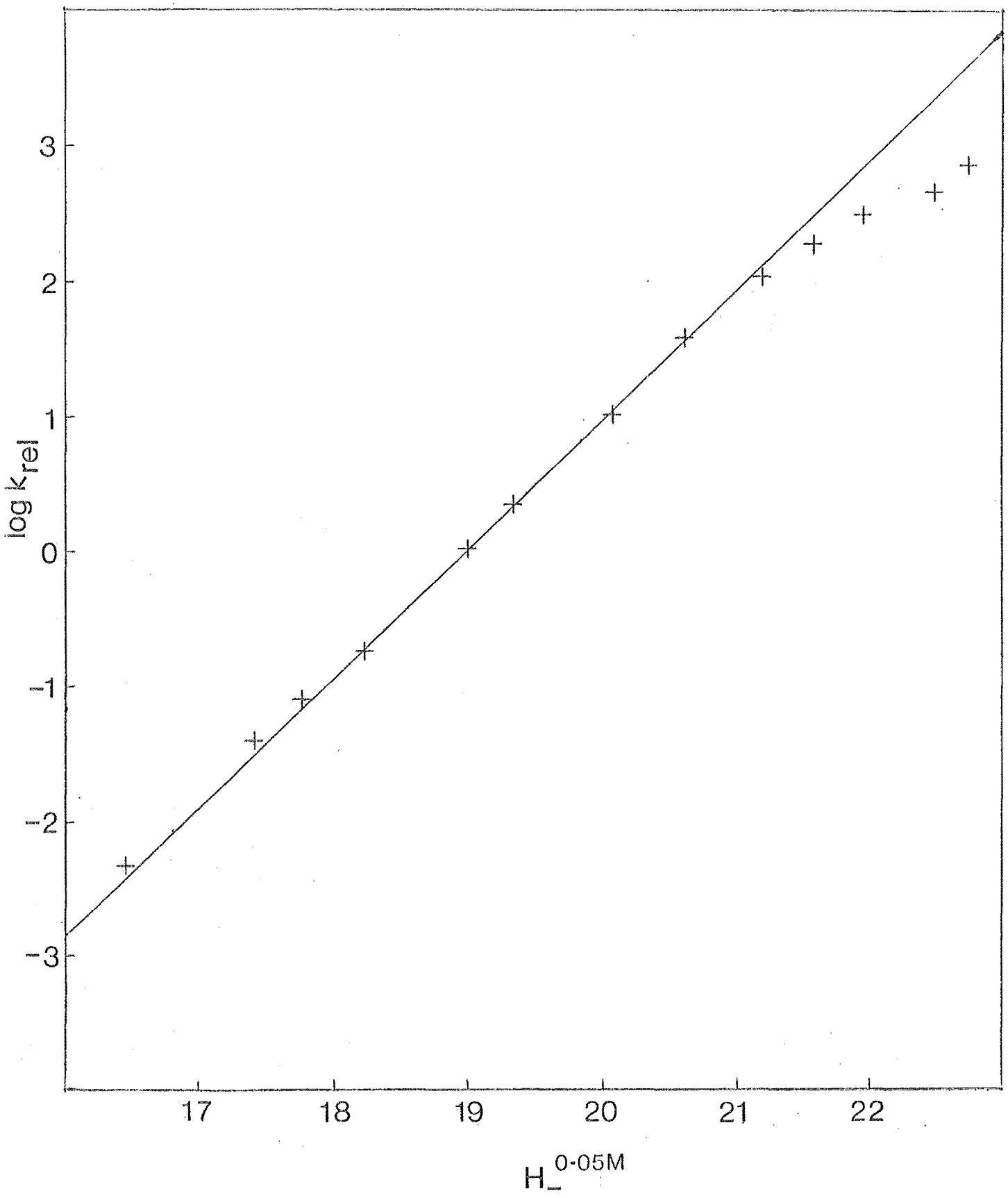


Fig. 20

Log k_{rel} vs $H_-^{0.05M}$ for Cleavage of Aryltrimethylsilanes by 0.05M KOH in Aqueous DMSO

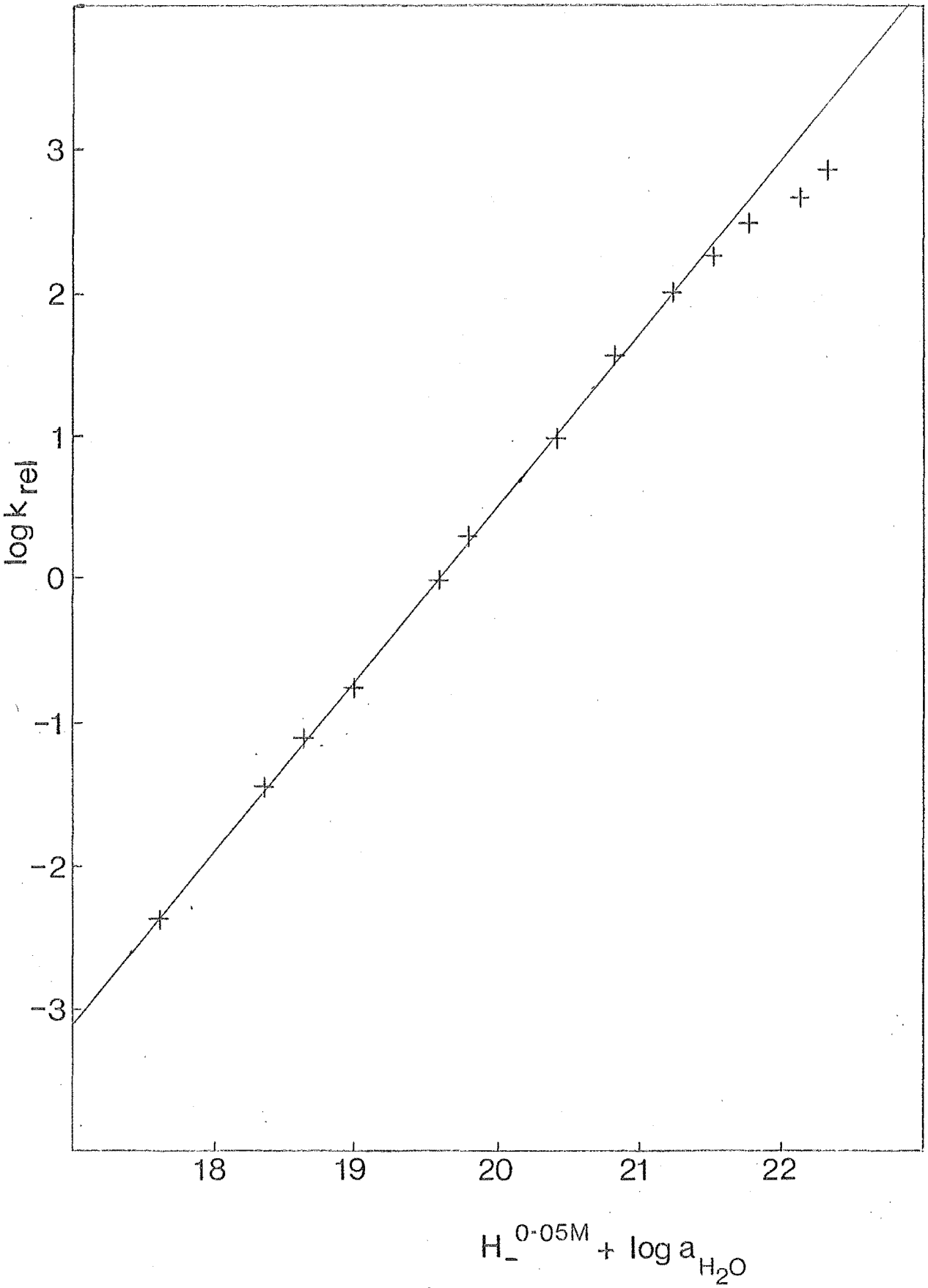


Fig. 21

Log k_{rel} vs $H_-^{0.05M}$ + log a_{H_2O} for Cleavage of Aryltrimethylsilanes by 0.05M KOH in Aqueous DMSO

between log k_{rel} and H_- + $\log_{10} a_{H_2O}$, with slope 1.20, a 10^5 variation in reactivity (see Fig. 21). The deviation above 95% v/v DMSO may arise because DMSO is hygroscopic; absorption of water probably occurs sufficiently to have a marked effect on H_- values at low water concentrations since H_- changes rapidly with $[H_2O]$.

The excellent correlation between log k_{rel} and H_- + $\log_{10} a_{H_2O}$ over a wide range of reactivity, and the near unity slope are consistent with hydroxide ion acting as a base in the rate determining step, abstracting a trimethylsilyl group rather than a proton from carbon. In proton removal, it is thought that the unity slope may be interpreted as showing almost complete bond formation between proton and base in the transition state[81]. If the same holds for removal of a trimethylsilyl group, the results are consistent with a mechanism in which the rate determining step is separation of Me_3SiOH from the aromatic centre, since in such a mechanism, bond formation with base is complete.

One criticism levelled at establishing a relationship of this sort, is that the H_- scale is highly dependent on the indicators used, in this case substituted anilines. In a situation such as the one considered here, the indicator and substrate structures differ markedly, and the assumption $\frac{f_{A^-}}{f_{AH}} \approx \frac{f_{\neq}}{f_{SH}}$, if it is true, will only be so fortuitously. However, it has been shown that a similar H_- scale results using carbon acids as indicators[81].

RATE DEPENDENCE ON [OH^-]

The rate of cleavage of 2-thienyltrimethylsilane in $33\frac{1}{3}$% v/v H_2O/DMSO is first order in KOH at low concentration, but above 0.10M increases to order 1.25 between 0.4M and 0.6M (see Table 9). H_- values for aqueous alkaline DMSO media in which [OH^-] alone is varied have not been measured, but this rate increase can be explained. In aqueous DMSO, there is strong hydrogen bonding between H_2O and DMSO, especially above $33\frac{1}{3}$ mole percent DMSO (i.e. below $33\frac{1}{3}$% v/v H_2O/DMSO)[26]. As [OH^-] increases, the degree of solvation of OH^- decreases because of competition between DMSO and OH^- for water molecules. As a result, the nucleophilicity of OH^- (or any other small anion) increases. At much higher [OH^-], (or lower mole percent water) nucleophilicity diminishes because of limited solubility in the medium. For example, in 10% v/v H_2O/DMSO, the reaction is less than first order in KOH between 0.10M and 0.20M (see Table 5). As mentioned later, some difficulty was experienced preparing such 0.20M solutions.

CLEAVAGE BY OTHER NUCLEOPHILES

Earlier it was shown that nucleophilicity is a function of both basicity and polarizability. In protic solvents, polarizability is more important; basic species, notably small anions, are highly solvated because of hydrogen bonding with the solvent. In aprotic solvents the situation is reversed; solvation occurs through interactions depending on polarizability, not hydrogen bonding, so that large polarizable anions are more effectively solvated than small anions.

As Table 10 shows, strong bases such as OH^-, MeO^-, NH_2^-, H^- and PhO^- rapidly cleave 2-thienyltrimethylsilane in DMSO at 40°C. Weakly basic species such as I^-, Br^- and SCN^- would not cleave this substrate even after 40 hours at 70°C. The order of nucleophilicity is:

$$OH^- > MeO^- > NH_2^- > H^- > PhO^- > CN^- > I^-, Cl^-, Br^-, N_3^-, SCN^-, NEt_3.$$

Reaction appears to be facilitated if 10% v/v H_2O/DMSO is used as a solvent instead of DMSO (Table 11).

Mass spectroscopic studies of the reaction products from the cleavage of trimethyl(m-chlorophenyl)silane and 2-thienyltrimethylsilane in KOH/DMSO confirmed the presence of hexamethyldisiloxane by the distinctive (P-15) peak at m/e = 147 [86]. The presence of trimethylsilanol could not be established as solvent obscured the spectrum. In earlier work[87] it was found that p-trimethylsilylbenzyltrimethylsilane was cleaved quite readily by fluoride ion in DMSO. The main by-product proved to be hexamethyldisiloxane, not fluorotrimethylsilane. However, fluorotrimethylsilane is known to hydrolyse to tri-

methylsilanol which readily condenses[88].

$$Me_3SiF + H_2O \rightleftharpoons Me_3SiOH + HF$$

$$2Me_3SiOH \rightleftharpoons (Me_3Si)_2O + H_2O.$$

The extent of cleavage by the nucleophiles listed in Tables 10 and 11 was determined by following the appearance of the product(s) containing the trimethylsilyl group by n.m.r. It appears from the positions of these peaks that common products occur in the reactions when carried out in DMSO or aqueous DMSO. One major product appears to be formed in cleavage by OH^-, MeO^- and O_2^{2-}, and a pair of different products in cleavage by other nucleophiles. From mass spectroscopic studies, the former product is undoubtedly hexamethyldisiloxane; the latter were not identified, although one may be trimethylsilanol.

In 5% v/v MeOH/DMSO, there is clear evidence that Me_3SiOMe is formed (≈ 60%) as well as $(Me_3Si)_2O$ (≈ 40%) when 2-thienyltrimethylsilane is cleaved by MeO^-; the mass spectrum of the product shows a distinctive (P-15) peak at m/e = 89 [86]. This product could arise from condensation of Me_3SiOH with methanol[89], although further investigation verified that MeO^-, not OH^-, was the active nucleophile. The rate of cleavage of trimethyl(p-nitrophenyl)silane by 0.1M MeONa in 10% v/v MeOH/DMSO is more noticeably accelerated by the addition of water than is the cleavage of the same species by 0.1M KOH, even though KOH cleaves almost twice as fast. This suggests that different nucleophiles are active in each case. Also, if there was enough water present to convert sufficient MeO^- to OH^- (i.e. ≈ 0.06M) to explain the observed rate, such an amount of water should have been noticeable in the n.m.r.

However, the n.m.r. spectrum of the MeOH/DMSO medium showed no trace of water. Little emphasis should be put on the nature of the products formed because of equilibria possible between products, and the ease with which many trimethylsilyl derivatives condense.

Difficulties arise in interpreting these results because the attacking species in many of the reactions could be hydroxide ion resulting from the equilibrium

$$X^- + H_2O \rightleftharpoons HX + OH^-$$

since DMSO is hygroscopic. In 10% v/v H_2O/DMSO, the higher concentration of water would increase the equilibrium hydroxide ion concentration, explaining the accelerated cleavage. However, this explanation is unlikely for two reasons. Firstly, the equilibrium would lie strongly to the left because little 'free' water is present - the water is bound up with DMSO. Secondly, the order of nucleophilicity should correlate with the basicities of the species, as measured by the pK_as of their conjugate acids. Although strong bases such as OH^-, MeO^-, NH_2^- and H^- are the best nucleophiles, this order is not followed; both OH^- and MeO^- are more reactive than the more basic NH_2^- and H^-, and PhO^- is noticeably more reactive than CN^- (see Table 10). In aqueous DMSO weak bases such as NH_3, OCl^- and AcO^- react to some extent, and F^-, a weak base, is a good nucleophile (see Table 11). Compared with stronger bases, the high reactivity of species such as F^- is not consistent with hydroxide ion acting as the sole nucleophile. The increased reactivity of the nucleophiles in aqueous DMSO can be attributed to greater solubility, as most are only marginally soluble in DMSO.

The most reasonable explanation of the observed order is that nucleophilicity is governed not only by the basicity of the species, i.e. its ability to donate a pair of electrons for bond formation, but also by the strength of the bond formed. Fluoride ion, and species containing nucleophilic oxygen, are more reactive than might be expected from their pK_a values. As Table 27 shows, fluorine and oxygen form particularly strong bonds with silicon.

Table 27

Ionic Bond Energies[1]

Bond	Energy(kJ/mol)	Bond	Energy(kJ/mol)
Si-C	932	Si-Br	748
Si-O	1014	Si-I	700
Si-F	992	Si-S	805
Si-Cl	796	Si-H	1042

One would expect H^- to be the best nucleophile since hydrogen forms the strongest bond with silicon, however H^- and NH_2^- are sufficiently basic to abstract a proton from DMSO (pK_a ~ 32) to form the dimsyl ion.[90]

dimsyl ion

If traces of water are present, hydroxide ion is formed

Hence it appears that small compact species such as OH^-, H^-, F^- and MeO^- are the best nucleophiles for cleaving the aryl-silicon bond; their reactivity is greatly enhanced in dipolar aprotic solvents such as DMSO because of the absence of solvation. With the exception of F^-, most such nucleophiles are highly basic, so there is a degree of correlation with the pK_a values of the conjugate acids of the nucleophiles. The strength of the bond formed is also an important factor, as might be expected if the mechanism involves bond formation in an equilibrium or rate determining step.

CLEAVAGE BY SODIUM METHOXIDE

Except for potassium hydroxide, the only other nucleophilic species whose behaviour could be readily studied was sodium methoxide, which in 5% v/v MeOH/DMSO, cleaved about 1.6 times slower than potassium hydroxide. For example, k_p = 5.04×10^{-2} min^{-1} for the cleavage of m-$BrC_6H_4SiMe_3$ by 0.03M KOH, while for cleavage by 0.03M MeONa, $k_p = 3.05 \times 10^{-2}$ min^{-1} (see Tables 12,14). This rate difference correlates with the difference in basicity between OH^- and MeO^- since $pK_a^{H_2O} - pK_a^{MeOH}$ = 15.74 - 15.50 = 0.24 and

$$\log k_{rel}^{OH^-} - \log k_{rel}^{MeO^-} = \log \frac{5.04 \times 10^{-2}}{3.05 \times 10^{-2}} = 0.22.$$

As in cleavage by KOH in aqueous DMSO, the rate dependence on nucleophile is greater than first order; over the range 0.03M to 0.27M MeONa in 5% v/v MeOH/DMSO, the reaction is order 1.35 in methoxide ion (see Table 13). This high dependence, compared with that of KOH in aqueous DMSO (between order 1 and 1.25) can be largely attributed to the solvent rather than the nucleophile, since hydroxide ion in 5% v/v MeOH/DMSO shows

even higher (order ~1.8) dependence (see Table 12). These effects probably arise because methanol is less protic than water; hence the absence of solvation is more marked in methanolic DMSO than aqueous DMSO.

A limited range of substituents was cleaved by both KOH and MeONa in 5% v/v MeOH/DMSO (see Tables 12,14). The patterns of substituent effects are very similar, and there is excellent correlation between the two sets of results.

$$\log k_{rel}^{MeO^-/MeOH} = 1.015 \log k_{rel}^{OH^-/MeOH} + 0.010 \quad (f = 0.022)$$

The near unity slope indicates that the sensitivity of the reaction to substituent changes is not influenced by the nucleophile involved, despite the greater overall nucleophilicity of hydroxide ion. The log k_{rel} values for both reactions also correlate well with those derived from cleavage by KOH in 10% v/v H_2O/DMSO.

$$\log k_{rel}^{MeO^-/MeOH} = 1.054 \log k_{rel}^{OH^-/H_2O} + 0.052 \quad (f = 0.108)$$

$$\log k_{rel}^{OH^-/MeOH} = 1.039 \log k_{rel}^{OH^-/H_2O} + 0.046 \quad (f = 0.098)$$

The greater than unity slope in both cases, shows that the reaction is slightly less sensitive to substituent changes in 10% v/v H_2O/DMSO than 5% v/v MeOH/DMSO. As mentioned earlier, dipolar aprotic solvents solvate large diffuse anionic species such as the transition state of the reaction being studied; hence 5% v/v MeOH/DMSO should solvate the transition state more effectively than 10% v/v H_2O/DMSO. The results are consistent with this, since the more stable the transition

state, the greater the sensitivity to substituent changes.

If nucleophilic attack at silicon were to occur in the rate determining step (either in a synchronous reaction, or to form an intermediate) one would expect variation of the nucleophile to have some influence on the pattern of substituent effects, although there are no such cases in the literature to illustrate this. However, the rate dependence on nucleophile rules out any mechanism in which the rate determining step is completely independent of the nucleophile. The most reasonable mechanism consistent with the results is that already suggested; rapid equilibrium formation of an intermediate, followed by rate determining decomposition of the intermediate to products.

REACTION IN OTHER SOLVENTS

Although the aryltrimethylsilanes synthesized could all be cleaved by KOH in aqueous DMSO, not even the most reactive substrate could be cleaved in media where DMSO was absent. 2-Thienyltrimethylsilane was not cleaved by 0.20M KOH in 10% v/v H_2O/MeOH, 10% v/v H_2O/acetone, or 10% v/v H_2O/DMF, even after several days at 40°C. By contrast, the half life in 10% v/v H_2O/DMSO is about 10^{-1} seconds. No reaction would be expected in aqueous methanol which would extensively solvate hydroxide ion, but both acetone and DMF are dipolar aprotic solvents with similar solvent properties to DMSO. For example, acetone, DMF and DMSO all enhance S_N2 substitution of n-butylbromide by azide ion, and nucleophilic aromatic substitution of para-fluoronitrobenzene by azide ion[23] (see Table 28).

Table 28

Relative Rates for Bimolecular Substitution Reactions in Various Solvents[23]

Solvent	$\log \frac{k_{solvent}}{k_{MeOH}}$ (measured at 25°C)	
	$\underline{n}$-BuBr + N_3^- →	$\underline{p}$-$NO_2C_6H_4F$ + N_3^- →
DMSO	3.1	3.9
DMF	3.4	4.5
acetone	3.6	4.9

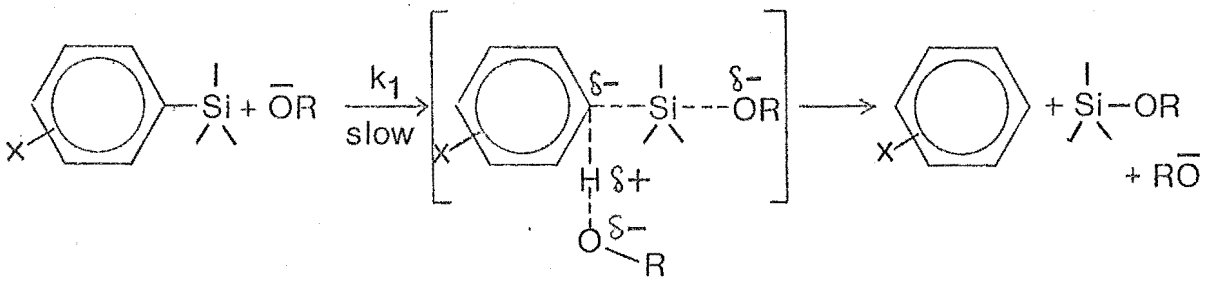
Both reactions involve rate determining nucleophilic attack so the comparable rates in the three solvents might suggest that enhanced nucleophilicity of species such as azide ion, is an inadequate basis for explaining the role of DMSO in the cleavage of aryltrimethylsilanes. However, other factors must be important in aryltrimethylsilane cleavage, because it has already been established that the reaction rate is linearly dependent on the basicity of the medium, and azide ion is a very weak base (pK_a = 4.62). Unfortunately, basicity functions in media such as H_2O/DMF and H_2O/acetone have yet to be reported. It is thought that DMSO is more basic than DMF or acetone. From the influence of aprotic solvents, both on the displacement of the ≡C - H absorption band in the i.r. spectrum of phenylacetylene[91], and on the proton shift in the n.m.r. spectrum of chloroform[92], the basicity order hexamethylphosphoramide > DMSO > DMF > acetone has been established. Hence water should hydrogen bond more strongly with DMSO than with DMF or acetone, to give media of higher basicity because of less solvation of bases such as OH^-.

Until basicity functions for such media as hydroxide ion in H_2O/DMF, H_2O/acetone and H_2O/hexamethylphosphoramide are established, one can only speculate as to whether differences in basicity are sufficient to explain the large ($> 10^6$) rate difference for reaction in aqueous DMSO compared with other media, evident in the results.

CONCLUSIONS

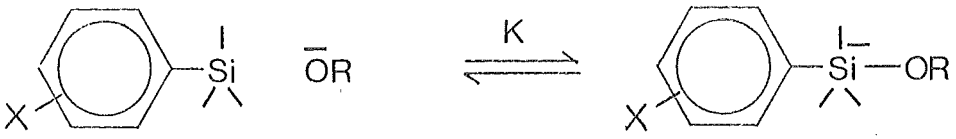
The pattern of substituent effects in the KOH cleavage of substituted phenyltrimethylsilanes in aqueous DMSO is best explained by a mechanism in which separation of a phenyl carbanion, accompanied by electrophilic attack by solvent, takes place in the rate determining step. Such a path is also supported by evidence in the literature, especially the sizeable isotope effects observed in the cleavage of phenyltrimethylstannanes, and benzyltrimethylsilanes and -stannanes. Of the possible mechanisms already outlined (see Introduction) two are consistent with the observed results:

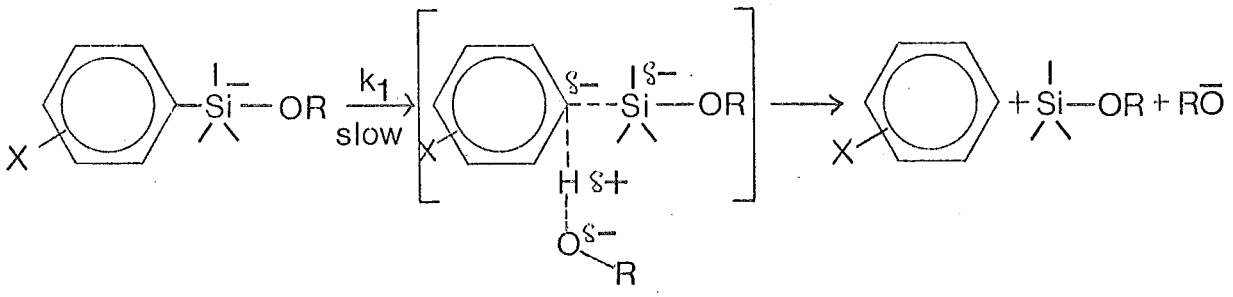
(i) an S_N2 mechanism in which nucleophilic attack and separation of a phenyl carbanion (with electrophilic assistance) are more or less synchronous.



$$\text{rate} = k_1[RO^-][ArSiMe_3][ROH]$$

(ii) a mechanism involving equilibrium intermediate formation followed by rate determining separation of a phenyl carbanion (with electrophilic assistance).





$$\text{rate} = k_1K[RO^-][ArSiMe_3][ROH]$$

Although the mechanisms cannot be distinguished kinetically, silicon is able to utilize the vacant 3d orbitals for bonding, and most evidence, especially stereochemical evidence, points to intermediate formation. However, apart from the racemization of trialkylfluorosilanes[59], there is no positive evidence for an initial equilibrium step. Exchange studies, for example the cleavage of $ArSiMe_2O^{18}Me$ by MeO^-, could provide more substantial evidence.

The correlation between rates and the acidity function H_- shows the importance of anion basicity, although stability of the bond formed between silicon and the nucleophile is also important, as shown by the reactivity of fluoride ion, a weak base.

The unique ability of DMSO to facilitate the reaction cannot be satisfactorily explained, as all dipolar aprotic solvents are known not to solvate small nucleophiles so enhancing their reactivities. It is known that DMSO is a stronger proton acceptor (i.e. is more basic) than solvents such as acetone or DMF, so that DMSO/protic mixtures are less solvating towards nucleophiles than comparable acetone or DMF mixtures.

EXPERIMENTAL

All ultraviolet spectrophotometry was carried out on a Shimadzu MPS-50L spectrophotometer fitted with an electronically thermostatted cell holder. N.m.r. spectra were recorded on a Varian A-60, mass spectra on an AEI MS 902, and infrared spectra on either a Shimadzu IR-27G or a Perkin-Elmer 337. Analytical gas chromatography was carried out on a Varian Aerograph 1200, and preparative gas chromatography on an Aerograph Autoprep 705. A Nester Faust 5 mm x 55 cm annular Teflon spinning band column was used for the fractional distillation of compounds for kinetics.

A. KINETIC RUNS

The cleavage reactions studied displayed kinetics first order in aryltrimethylsilane.

i.e. $\text{rate} = k_p[ArSiMe_3]$

where k_p is the pseudo first order rate constant $k_p = k[OR^-]^n$.

Reaction was followed by either (i) ultraviolet spectrophotometry or (ii) n.m.r. spectroscopy.

(i) Ultraviolet Spectrophotometry

In the simplest form, the reaction studied can be written as

$$Ar-SiMe_3 + OR^- \xrightarrow{ROH} Ar-H + Me_3Si-OR + OR^- \qquad (1)$$

R = H, Me

where the only species absorbing in the ultraviolet region are the aryltrimethylsilane ($ArSiMe_3$) and the corresponding arene (Ar-H). The rate of cleavage can therefore be followed at a

wavelength at which the two extinction coefficients differ significantly. Although the absorbances of both species are changing, the overall rate constant measured represents the rate constant for the cleavage of silane, as the following analysis shows.

The disappearance of reactant can be written as

$$[R]_t = [R]_0 e^{-k_p t} \tag{2}$$

where $[R]_t$ is the reactant concentration at time t, $[R]_0$ is the initial reactant concentration, and k_p is the pseudo first order rate constant. Unless a buildup of intermediate occurs, the appearance of product must occur at the same rate, so that

$$[P]_t = [P]_f(1-e^{-k_p t}) \tag{3}$$

where $[P]_t$ is the product concentration at time t and $[P]_f$ is the final product concentration. The absorbance of a species is related to its concentration;

$$A_{R(t)} = [R]_t \cdot \varepsilon_R \cdot \ell_R \tag{4}$$

where $A_{R(t)}$ is the absorbance of the reactant at time t, ε_R is the reactant extinction coefficient and ℓ_R is the cell path length. Similarly

$$A_{P(t)} = [P]_t \cdot \varepsilon_P \cdot \ell_P \tag{5}$$

Substituting (4) into (2), and (5) into (3) gives

$$A_{R(t)} = A_{R(o)} e^{-k_p t} \tag{6}$$

$$A_{P(t)} = A_{P(f)}(1 - e^{-k_p t}) \tag{7}$$

From (6) and (7), the net absorbance at time t can be expressed as

$$A_{R(t)} + A_{P(t)} = A_{P(f)} + (A_{R(o)} - A_{P(f)})e^{-k_p t} \quad (8)$$

So the rate constant k_p is common to the disappearance of reactant and the change in the net absorbance of the two species.

Procedure

Direct mixing of DMSO and OR^-/ROH solutions to initiate kinetics was unsatisfactory because of an initial cloudiness in the resulting solutions which upset absorbance measurements, so a technique involving pre-mixing was adopted. The X% v/v ROH/DMSO solutions were prepared by mixing X volumes of OR^-/ROH and 95-X volumes of DMSO, and the solutions allowed to clear (this usually took several hours at 40°C). A solution of the appropriate aryltrimethylsilane in DMSO was also prepared; the concentration of this solution being twenty times the concentration necessary to give an absorbance of about 0.8 at the chosen wavelength.

Runs were carried out as follows. The OR^-/ROH/DMSO medium was stored in a water bath at 40.0°C; 2 mls of the medium was then pipetted into a 1 cm silica absorption cell and brought to 40.0°C. 105 Microlitres of the aryltrimethylsilane/DMSO solution (also stored at 40.0°C) was then added from a syringe, and the mixture shaken. Fast reactions were run in the spectrophotometer with the cell compartment thermostatted at 40.0°C, and the absorbance continuously recorded. For slow reactions, the cell was kept in a constant temperature bath at 40.0°C and rapidly transferred to the

thermostatted cell compartment of the spectrophotometer at appropriate intervals for measurement. All reactions were followed for 3-4 half lives except for the two least reactive compounds (m-$Me_2NC_6H_4SiMe_3$ and p-$Me_2NC_6H_4SiMe_3$) which were followed for two half lives. Wavelengths used may be found in Tables 5 and 7.

(ii) N.m.r. Spectroscopy

It was not possible to follow the cleavage of 2-furyltrimethylsilane in the ultraviolet, as the reactant does not absorb significantly above 250 nm, and the reaction medium is opaque below 250 n.m. However, cleavage of 2-furyltrimethylsilane shifts the trimethylsilyl peak in the n.m.r. sufficiently upfield to allow the relative quantities of reactant and products (Me_3SiOR and hexamethyldisiloxane) to be determined by integration of their respective trimethylsilyl peaks. This made it possible to follow the cleavage of 2-furyltrimethylsilane by n.m.r. spectroscopy using the procedure outlined below. Cleavage of 2-thienyltrimethylsilane was also monitored by n.m.r. to check if the results were consistent with those obtained by the u.v. method.

Procedure

A volume (usually 5 mls) of the reaction medium X% ROH/DMSO, prepared by mixing X volumes of OR^-/ROH and 100-X volumes of DMSO, was placed in a vial sealed with a rubber septum, and brought to 40.0°C in a constant temperature bath. To initiate reaction, a quantity of reactant was injected into the vial and the mixture shaken. At appropriate intervals, 0.5 millilitre aliquots were withdrawn and quenched with 0.4 ml methanol in an n.m.r. tube. For most runs, 10 samples were taken over 3-4 half lives. The spectra of the samples in the region

20 cps to -30 cps (relative to TMS) were recorded, and the peaks present integrated at least eight times.

B. ANALYSIS OF KINETIC DATA

All reactions studied were carried out under pseudo first order conditions, using $[OR^-] > 10[ArSiMe_3]$. Kinetic data were analysed with a least squares computer program, an adaption of the ORGLS program[93]. The program fits a calculated first order curve to the experimentally obtained curve by varying the parameters of a function for first order decay. The criterion for fitting the curve is the minimization of the sum of the squares of the differences between actual and calculated observations. For reactions followed by the u.v. method, the function is

$$A_t = A_\Delta e^{-k_p t} + A_f$$

where A_t is the calculated absorbance at time t, A_Δ is the net absorbance change during reaction, and A_f is the final absorbance. Data input consisted of approximate values of the three parameters A_Δ, A_f and k_p, and a set of observed absorbances with their times. Usually fourteen observations, all equally weighted, were taken at increasing intervals over four half lives. Approximate values of k_p were obtained from the data by the Guggenheim method[94].

For reactions followed by n.m.r., the trimethylsilyl peaks were integrated at least eight times per sample, and from the integrations, mole percentages of reactant present determined. The mean percentage of reactant in each sample was calculated, and the standard deviation of the mean calculated using the formula

$$\sigma = \sqrt{\frac{\sum_i (\chi_i - \bar{\chi})^2}{(N-1)}}$$

where χ_i is the observed percentage of reactant, $\bar{\chi}$ is the mean percentage of reactant, and N is the number of integrations. Data was analysed by the least squares program using the function

$$P_t = P_\Delta e^{-k_p t} + P_f$$

where P_t is the percentage of reactant at time t, P_Δ is the change in the percentage of reactant during the reaction, and P_f is the final percentage of reactant. Ideally, $P_\Delta = 100$, and $P_f = 0$; however, these parameters were varied to allow for any extraneous n.m.r. signals.

Data input consisted of approximate values of P_Δ, P_f and k_p, and a set of observed mean percentages of reactant, (weighted according to their standard deviations) and their times. Usually ten observations were taken at increasing intervals over 3-4 half lives.

Analysis using the program yielded estimated values of the parameters, and their errors, as well as a set of calculated data points and the standard deviation of the fitted curve. A sample u.v. kinetic run and its analysis is shown in Appendix A.

Sources of Error

1. Reagents

For all kinetic work, AR grade KOH and Koch-Light "puriss" sodium methoxide was used. Any errors due to impurities should be systematic and eventually cancel in the calculation of relative rates.

2. Volumetric Measurements: Errors from pipetting (either in preparing reaction media or initiating kinetic runs) should be systematic; the same equipment was used throughout.

3. Temperature Control: Runs were carried out at 40.0°C, either in a water bath controlled to ∓ 0.05°C by a Tempunit, or in a thermostatted cell within the u.v. spectrophotometer controlled to ∓ 0.1°C.

4. Time: For reactions followed by u.v., time errors were negligible; for fast reactions an accurate stopwatch was used both to calibrate the scanning speeds of the spectrophotometer, and to record the time necessary to initiate runs. For slow reactions, the same stopwatch was used to record the times at which absorbances were measured.

For reactions followed by n.m.r., the conditions of reaction were adjusted so that the rate was slow enough for the several seconds time delay in quenching samples to be insignificant. The quenching technique adopted was shown to be effective; spectra of the quenched samples were run within a few hours, and it was found that negligible reaction occurred in samples over three days.

5. Absorbance by the reaction medium: A blank was run with most reactions followed by u.v., and the absorbance of the medium seldom changed by more than 0.01 during the course of a run; the observed absorbances were corrected accordingly.

6. Calculation of rate constants: In u.v. runs, observed absorbances were read from data to within ∓ 0.001, and the corresponding calculated absorbances derived by the program usually lay as close as this to the observed values. The standard error in the rate constant k_p was usually greatest in runs covering a

long period, or where the absorbance change to be followed was small. Runs were usually carried out in triplicate with good reproducibility; the standard deviation ($\bar{\sigma}$) of the estimate of the mean rate constant ($\bar{k}_p$) was usually comparable with the standard error (σ) of the individual k_p values (see Table 5).

Similarly, in n.m.r. runs, reproducibility was satisfactory although errors generally were much higher than in u.v. runs; in some cases a number of data points were rejected because they were greater than 3 standard deviations from the curve of best fit. As the cleavage of 2-thienyltrimethylsilane shows (Table 7), the u.v. and n.m.r. methods gave consistent results.

C. REACTION WITH OTHER NUCLEOPHILES, AND IN OTHER MEDIA

(i) Cleavage by nucleophiles in DMSO and 10% v/v H_2O/DMSO

Solutions of nucleophilic species in DMSO and 10% v/v H_2O/DMSO were prepared and 2 mls of each placed in vials which were sealed and placed in a water bath at 40°C or 70°C. Sodium phenoxide was generated by adding an appropriate quantity of $NaNH_2$ to 10% w/v PhOH/DMSO. 40 Microlitres of 2-thienyltrimethylsilane were introduced to each sample and the contents thoroughly mixed; ½ ml samples were then withdrawn at intervals and their n.m.r. spectra recorded to determine the extent of reaction. The position of the product trimethylsilyl peak in each case was also noted (see Tables 10,11).

(ii) Cleavage by nucleophiles in other solvents

Solutions (0.2M) of KOH in 10% v/v H_2O/DMF, 10% v/v H_2O/acetone, and 10% v/v H_2O/MeOH were prepared and 2 ml of each placed in vials which were sealed and placed in a water

bath at 40°C. The procedure outlined in (i) was followed.

D. REAGENTS

Dimethyl sulphoxide (Koch-Light) was redistilled off calcium hydride under reduced pressure at 80°C and stored over molecular sieves.

Methanol was dried over calcium oxide, redistilled off the Grignard reagent formed from magnesium and methanol, and stored over molecular sieves.

Dimethylformamide was dried by the azeotropic removal of water with benzene, redistilled, and stored over molecular sieves.

KOH, KCN, KSCN, KCl, KBr, KI, Na_2O_2, CH_3COONa and $NaNO_2$ were AR grade; MeONa, $NaNH_2$, LiH, KF (oven dried before use), NaN_3, NEt_3, K_2SiO_3, and NaOCl were pure grade.

E. PREPARATION OF ARYLTRIMETHYLSILANES

A series of substituted phenyltrimethylsilanes, $XC_6H_4SiMe_3$ (where X = m-, p-NO_2, m-CF_3, m-, p-Br, m-, p-Cl, m-, p-F, m-, p-Ph, m-, p-OMe, H, m-, p-Me, p-Et, m-, p-NMe_2) were prepared as outlined. The syntheses of 2- and 3-thienyltrimethylsilane and 2-furyltrimethylsilane are also described. Most compounds were prepared by the Wurtz reaction from chlorotrimethylsilane and the appropriate chloro or bromoarene, or by the Grignard reaction from chlorotrimethylsilane and the appropriate bromoarene. Grignard reactions were carried out under nitrogen in sodium dried ether or dry THF, using ethylene dibromide as an initiator, and a trace of iodine to indicate the beginning of Grignard formation. Compounds used

for kinetics were identified by their mass spectra, and by comparing their infrared spectra with spectra in the literature. Unless otherwise stated, all gave a single peak when checked for purity by gas chromatography on both 3% PDEAS/Aeropak 30 and 3% S.E. 30/Chromosorb G columns.

1. Trimethyl(m-nitrophenyl)silane

The Grignard reagent from m-bromochlorobenzene (30g) and magnesium (3.8g) in ether was reacted with excess chlorotrimethylsilane to give (m-chlorophenyl)trimethylsilane[95] (21g, 72%). This was treated with chlorotrimethylsilane (13.6g) and sodium (5.7g) in toluene to give, after work up and fractional distillation, m-bis(trimethylsilyl)benzene[95] (9.5g, 36%) b.p. 82°C/4mm. m-Bis(trimethylsilyl)benzene (5g) was nitrated[96], and the crude product partially purified on a filtration column of 5% deactivated alumina using ligroin as solvent, then fractionated to give 96% pure trimethyl(m-nitrophenyl) silane, (1.3g, 30%).

2. Trimethyl(p-nitrophenyl)silane was prepared by the method outlined in 1. p-Bromochlorobenzene (50.2g) gave (p-chlorophenyl)trimethylsilane, (17g, 35%) which, in turn, yielded after crystallization from methanol, p-bis(trimethylsilyl)benzene[95], (7.9g, 38%), m.p. 90-92°C, (lit., 89°C). 6.5g of this compound was nitrated[96] and the product recrystallized from ligroin, giving pure trimethyl(p-nitrophenyl)silane (0.3g, 5%), m.p. 35-36°C, (lit.[96], 37°C).

3. (m-Trifluoromethylphenyl)trimethylsilane

Excess chlorotrimethylsilane was added to the Grignard formed from m-bromo-α,α,α-trifluorotoluene (25g) and magnesium (2.7g) in 60 mls of ether, and the mixture refluxed overnight. The reaction mixture was hydrolysed with saturated ammonium

chloride solution, the organic phase separated, and the aqueous phase extracted several times with ether. The organic phase and the ether extracts were combined, washed once with water, dried over calcium chloride, and the solvent removed. Fractional distillation of the crude material gave pure (m-trifluoromethylphenyl)trimethylsilane, (4.3g, 18%), b.p. 61°C/10 mm, (lit.[97], 175.1°C/760 mm).

4. (m-Bromophenyl)trimethylsilane was prepared from m-dibromobenzene (20g) by the method outlined in 3[98]. The crude product was brominated in acetic acid to convert the main by-product, p-bis(trimethylsilyl)benzene, to (m-bromophenyl)trimethylsilane. Fractional distillation then gave pure (m-bromophenyl)trimethylsilane, (4.3g, 22%), b.p. 80°C/4 mm, (lit.[98], 75°C/1 mm).

5. (p-Bromophenyl)trimethylsilane[99] was prepared from p-dibromobenzene (100g) by the method outlined in 3. m-Bis-(trimethylsilyl)benzene was brominated with bromine in acetic acid and fractional distillation gave pure (p-bromophenyl)-trimethylsilane, (11.1g, 11%), b.p. 87°C/5.5 mm, (lit.[99], 146-148°C/50 mm).

6. (m-Chlorophenyl)trimethylsilane[95] was prepared from m-bromochlorobenzene (40g) by the method outlined in 3, but using THF as solvent. Fractional distillation gave pure (m-chlorophenyl)trimethylsilane, (15.2g, 40%), b.p. 80°C/8 mm, (lit.[95], 206-207°C/740 mm).

7. (p-Chlorophenyl)trimethylsilane[99] was prepared from p-bromochlorobenzene (50 g) by the method used in 3, but with THF as solvent. Fractional distillation gave pure (p-chlorophenyl)trimethylsilane, (14.2g, 30%), b.p. 78°C/7 mm, (lit.[99], 119-120°C/50 mm).

8. (m-Fluorophenyl)trimethylsilane was prepared from m-bromofluorobenzene (16g) by the method used in 3, but with THF as solvent. Fractional distillation gave pure (m-fluorophenyl) trimethylsilane, (5g, 33%), b.p. 58.5°C/11 mm.

9. (p-Fluorophenyl)trimethylsilane[100] was prepared from p-bromofluorobenzene (40g) by the method used in 3, but with THF as solvent. Fractional distillation gave pure (p-fluorophenyl)trimethylsilane, (17.6g, 46%), b.p. 54.5°C/10.5 mm, (lit.[100], 92-93°C/60 mm).

10. 3-Biphenylyltrimethylsilane was prepared from 3-bromobiphenyl (16g) by the method used in 3, but with THF as solvent. Fractional distillation gave pure 3-biphenylyltrimethylsilane (5.7g, 37%), b.p. 130°C/3.8 mm, (lit.[95], 138°/4mm).

11. 4-Biphenylyltrimethylsilane. A mixture of 4-bromobiphenyl (20g) and chlorotrimethylsilane (11g) in 25 mls of toluene was added dropwise to sodium (4.8g) in 50 mls of refluxing toluene[95]. When reaction was complete, acetic acid was added to destroy excess sodium and the mixture washed several times with sodium bicarbonate solution and once with water. The organic phase was dried over calcium chloride, the toluene removed by evaporation and the crude product recrystallised twice from methanol, giving pure 4-biphenylyltrimethylsilane, (5g, 26%), m.p. 51-52°C, (lit.[95], 50-51°C).

12. (m-Methoxyphenyl)trimethylsilane. m-Bromoanisole (20g) prepared in 45% yield from the methylation of m-bromophenol with dimethyl sulphate[101], was silylated by the method used in 3, but with THF as solvent. Fractional distillation gave pure (m-methoxyphenyl)trimethylsilane, (5.2g, 27%), b.p. 97°C/11 mm, (lit.[102], 216°C/751 mm).

13. (p-Methoxyphenyl)trimethylsilane[103] was prepared from p-bromoanisole (30g) by the method outlined in 3, but using THF as solvent. Fractional distillation gave pure (p-methoxyphenyl) trimethylsilane (19g, 66%), b.p. 92°C/7.6 mm, (lit.[103], 222.5°-223.5°C/760 mm).

14. Trimethylphenylsilane was prepared from chlorobenzene (40g) by the method outlined in 11. Fractional distillation gave pure trimethylphenylsilane (20.9g, 39%), b.p. 58°C/11.4 mm, (lit.[1], 171.5°C/760 mm).

15. Trimethyl-m-tolylsilane was prepared from m-bromotoluene (19.2g) by the method outlined in 11. Fractional distillation gave pure trimethyl-m-tolylsilane (4.9g, 20%), b.p., 70°C/11.5 mm, (lit.[95], 188°C/748 mm).

16. Trimethyl-p-tolylsilane was prepared from p-bromotoluene (25.6g) by the method outlined in 11. Fractional distillation gave pure trimethyl-p-tolylsilane (10g, 41%), b.p. 67°C/7.8 mm, (lit.[95], 192°C/748 mm).

17. (p-Ethylphenyl)trimethylsilane was prepared from p-bromoethylbenzene (27.7g) by the method outlined in 11. Fractional distillation gave pure (p-ethylphenyl)trimethylsilane (11g, 41%), b.p. 83°C/9mm (lit.[104], 207-208.5°C/760 mm).

18. N,N-Dimethyl-m-(trimethylsilyl)aniline. m-Bromo-N,N-dimethylaniline (18.2g) prepared in 32% yield by the methylation of m-bromoaniline with dimethyl sulphate[105], was reacted with chlorotrimethylsilane[106] by the method used in 3, but with THF as solvent. Fractional distillation gave pure N,N-dimethyl-m-(trimethylsilyl) aniline, (4.6g , 26%), b.p. 104°C/7.5 mm, (lit.[107], 59-60°C/0.4 mm).

19. N,N-Dimethyl-p-(trimethylsilyl)aniline was prepared from p-bromo N,N-dimethylaniline (9.7g) by the method used in 3 but

with THF as solvent[106]. Fractional distillation gave pure N,N-dimethyl-p-(trimethylsilyl)aniline, (2.6g, 28%).

20. 2-Thienyltrimethylsilane

n-Butyl-lithium, prepared from n-butyl-bromide (145g) and lithium (18.2g)[108], was reacted with thiophene (40g), then chlorotrimethylsilane (52g), after the method of Benkeser and Currie[109]. Fractional distillation of the crude product gave pure 2-thienyltrimethylsilane, (29.4g, 39%), b.p. 53°C/11 mm (lit.[109], 159-160°C/.748 mm).

21. 3-Thienyltrimethylsilane

Bromine (1080g) was added slowly to thiophene (188g) in 75 mls of chloroform[110]. The reaction mixture was washed with sodium hydroxide solution, then refluxed for six hours with potassium hydroxide (133g) in ethanol. After being washed with water and dried over sodium sulphate, the crude product was distilled to give 2,3,5-tribromothiophene, (467g, 66%), b.p. 140°C/20 mm (lit.[113], 123-124°C/9 mm), and 2,3,4,5-tetrabromothiophene (71g, 8%), b.p. 190°C/20 mm.

2,3,5-Tribromothiophene (267g) was added slowly to a refluxing mixture of zinc dust (163g), acetic acid (145 mls) and water (400 mls) and refluxing continued overnight. The reaction mixture was steam distilled, to give crude product (112g) which was dried and redistilled to give 98% pure 3-bromothiophene, (95g, 70%), b.p. 159-160°C/760 mm, (lit.[110], 159-160°/760 mm).

A mixture of ethylbromide (50g) and 3-bromothiophene (36g) in 500 mls of ether was added slowly to magnesium turnings (20g) in 150 mls ether and the resulting mixture refluxed overnight[79]. Chlorotrimethylsilane (100g) was added and refluxing continued for four hours. The reaction mixture

was worked up in the usual way to give crude product (49g) which was fractionated, yielding 3-thienyltrimethylsilane in five cuts ranging in purity from 95% to 100%. (5.2g, 15%), b.p. 172°C, (lit.[79], 168°C).

22. 2-Furyltrimethylsilane was prepared from furan (40g), n-butyl-lithium, and chlorotrimethylsilane by the route used for 2-thienyltrimethylsilane[109]. Fractional distillation gave 2-furyltrimethylsilane about 80% pure (6g, 7%), b.p. 124°C/760 mm, (lit., 124-125°C/750mm). The best fraction was purified by preparative gas chromatography, using a 25% Carbowax 20M/ Celite column. Two fractions (0.23g, 0.46g) were collected, the latter, 100% pure, was used for kinetics.

APPENDIX A

The following shows the steps involved in obtaining rate constants for base cleavage of aryltrimethylsilanes. The cleavage of (m-chlorophenyl)trimethylsilane is used as an example.

(i) The u.v. spectra of (m-chlorophenyl)trimethylsilane (2.16×10^{-3}M) and chlorobenzene (2.13×10^{-3}M) in DMSO (Fig. 22) show that the most suitable wavelengths to follow the reaction are 270 and 277 n.m.; the former was chosen.

(ii) 10% v/v H_2O/DMSO (2 ml) containing 0.1M KOH was added to a 1 cm silica cell and brought to 40.0°C using the thermostatted cell holder. To this, 4.66×10^{-2}M m-$ClC_6H_4SiMe_3$ (105 µl) in DMSO was added, the solution mixed, and the absorbance of the reaction mixture at 270 n.m. followed using an appropriate time scan (see Fig. 23). Allowance was made for the mixing time required.

(iii) Approximate values of the parameters A_f (final absorbance) and A_Δ (net absorbance change during reaction) were obtained by inspection from the curve. An approximate value of the other parameter k_p was obtained from a Guggenheim plot (not shown) which was an excellent straight line, indicating a first order reaction in substrate.

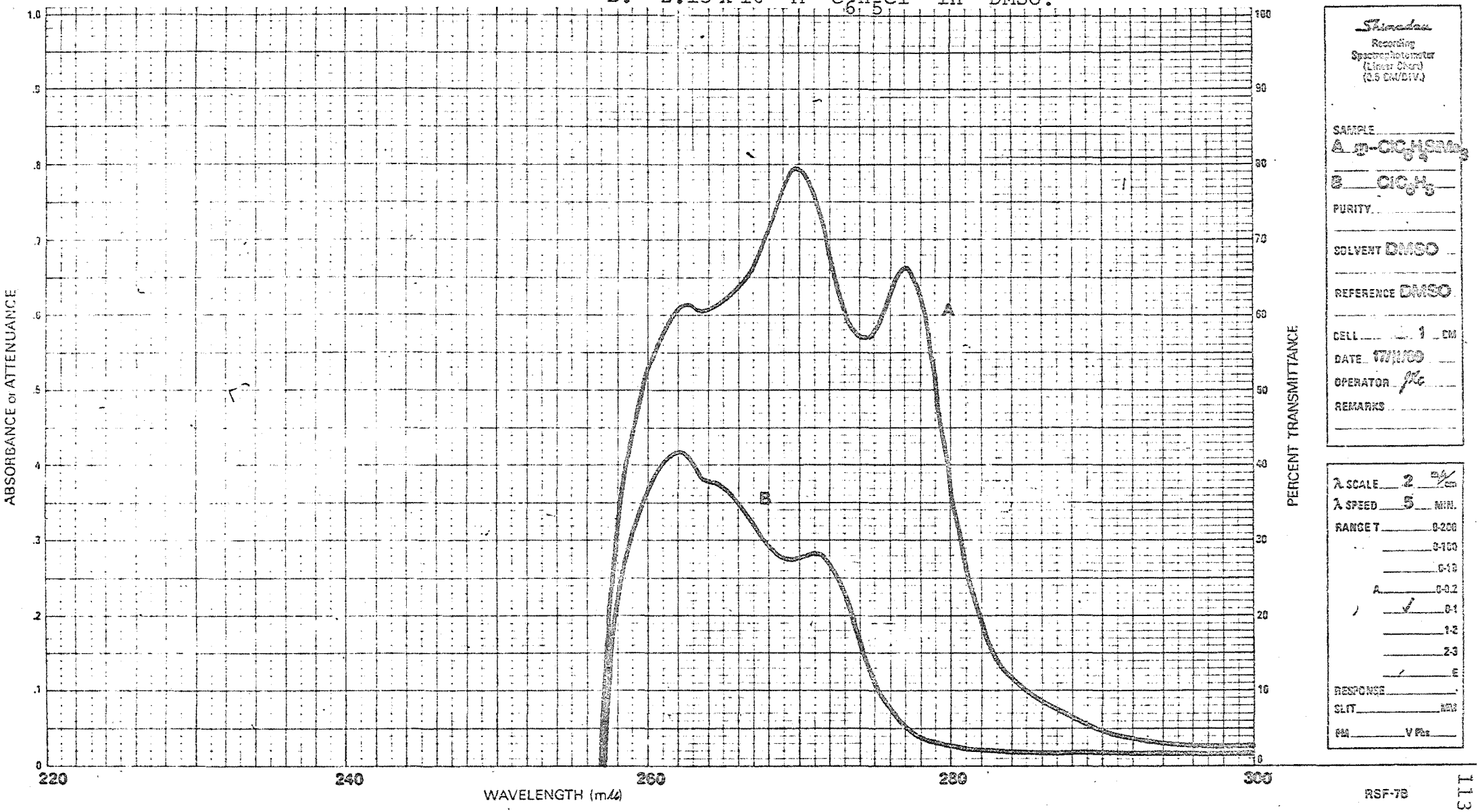
Note: A simpler method adopted later to find k_p is to estimate the half life ($t_{½}$) of the reaction, i.e. the time for the net absorbance to drop by 50%. Hence k_p can be found, since

$$k_p = \frac{\log_e 2}{t_{½}}$$

Fig. 22

Ultraviolet Spectra of A. 2.16×10^{-3} M m-$ClC_6H_4SiMe_3$ in DMSO

B. 2.13×10^{-3} M C_6H_5Cl in DMSO.



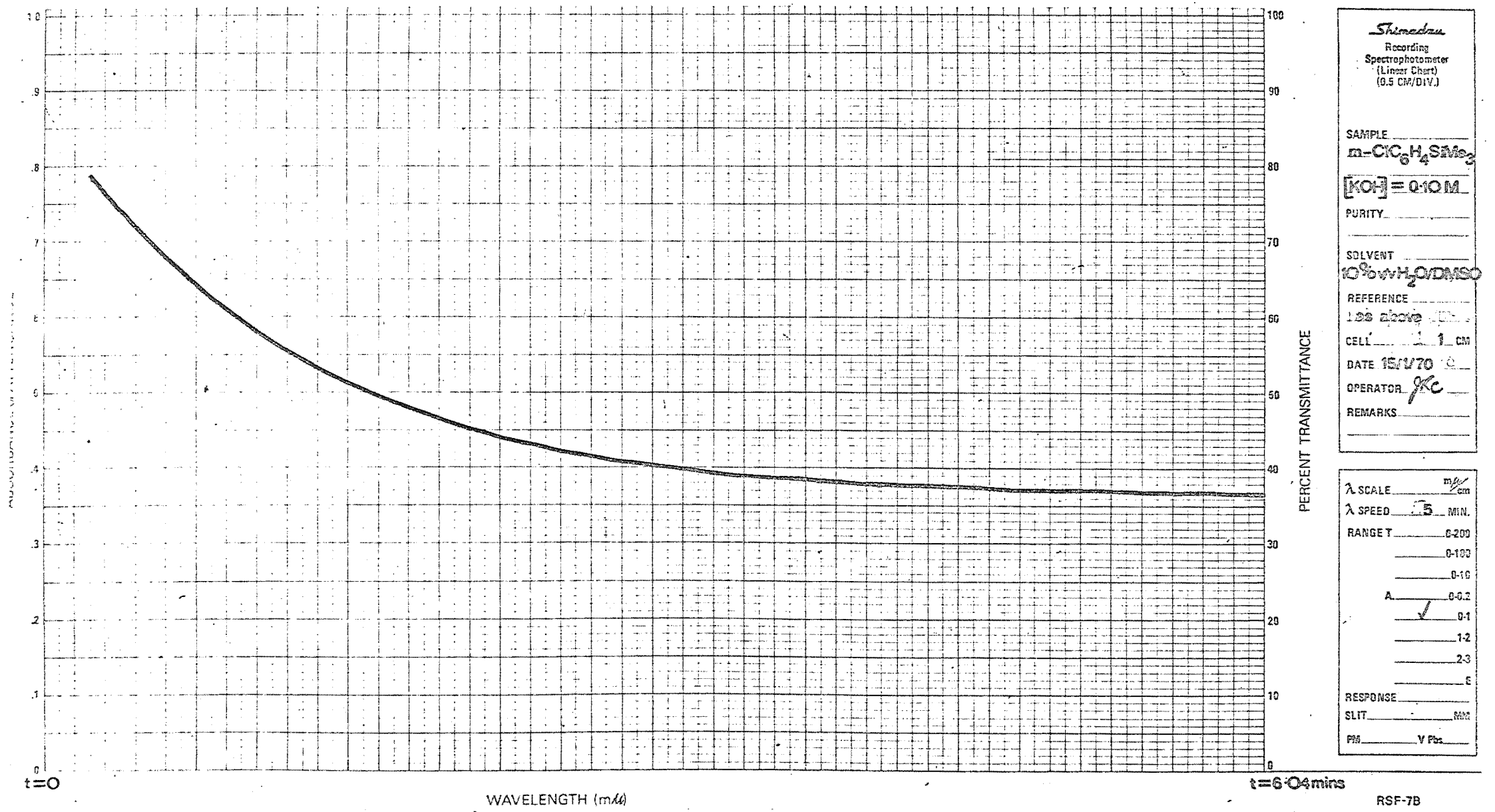


Fig. 23

Absorbance Curve for Cleavage of m-$ClC_6H_4SiMe_3$ by 0.10M KOH in 10% v/v H_2O/DMSO.

(iv) Input Data

Approximate parameter values:

1. A (x 1000) = 570
2. $k_p = 1.35 \times 10^{-1}$ sec^{-1}
3. A_f (x 1000) = 330

Table 29

Observed Absorbances

A^a_{obs} (x1000)	no. of divisions (cm)	Time/division[b] (sec/cm)
703	3	9.06
664	4	"
627	5	"
596	6	"
567	7	"
539	8	"
517	9	"
481	11	"
452	13	"
427	15	"
409	17	"
388	20	"
374	23	"

a. Adjusted for absorbance change in the medium during the reaction.

b. Since each scan is divided into cms, the program used to calculate results was modified to calculate the time of each observation as (secs/cm.) X (no. of cms at which the observation is taken.)

(v) Output

J.R. Cretney Base Cleavage M Chloro Run 5

Number of cycles in this job is 6.

Number of parameters to be varied is 3.

Number of independent variables per observation is 5.

Value of weighting constant is 0.0.

Derivatives programmed by user.

Unit weights to be set by program.

Parameters to be read as input data.

Corrected parameters not to be saved for later use.

Number of parameters read is 3.

Number of observations read is 13.

Input Data

I	P(I)	KI(I)	DP(I)
1	0.5700E 03	1	0.0
2	0.1350E-01	1	0.0
3	0.3300E 03	1	0.0

Agreement factors based on parameters before cycle 6.

Sum (W*(0-C)**2) is 0.108E 02.

SQRTF(Sum(W*(0-C)**2)/(NO-NV)) is 1.0368.

J.R. Cretney Base Cleavage M Chloro Run 5

Parameters after least squares cycle 6

	OLD	CHANGE	NEW	ERROR
1	0.5198E 03	-.7036E-04	0.5198E 03	0.1550E 01
2	0.1313E-01	-.5281E-09	0.1313E-01	0.1335E-03
3	0.3401E 03	0.3658E-04	0.3401E 03	0.1529E 01

J.R. Cretney Base Cleavage M Chloro Run 5

Calculated Y Based on Parameters Before Cycle 7

Y(OBS)	Y(CALC)	OBS-CALC	SIG(0)	(0-C)/SIG(0)	X(1)	X(2)	X(3)	CT.TIME	BKGRD
703.0000	703.9446	-0.9446	1.0000	-0.9446	27.	3.0000	9.0600	0.0	0.0
664.0000	663.1406	0.8594	1.0000	0.8594	36.	4.0000	9.0600	0.0	0.0
627.0000	626.9128	0.0872	1.0000	0.0872	45.	5.0000	9.0600	0.0	0.0
596.0000	594.7483	1.2517	1.0000	1.2517	54.	6.0000	9.0600	0.0	0.0
567.0000	566.1914	0.8086	1.0000	0.8086	63.	7.0000	9.0600	0.0	0.0
539.0000	540.8369	-1.8369	1.0000	-1.8369	72.	8.0000	9.0600	0.0	0.0
517.0000	518.3264	-1.3264	1.0000	-1.3264	82.	9.0000	9.0600	0.0	0.0
481.0000	480.5962	0.4038	1.0000	0.4038	100.	11.0000	9.0600	0.0	0.0
452.0000	450.8545	1.1455	1.0000	1.1455	118.	13.0000	9.0600	0.0	0.0
427.0000	427.4102	-0.4102	1.0000	-0.4102	136.	15.0000	9.0600	0.0	0.0
409.0000	408.9297	0.0703	1.0000	0.0703	154.	17.0000	9.0600	0.0	0.0
388.0000	388.2795	-0.2795	1.0000	-0.2795	181.	20.0000	9.0600	0.0	0.0
374.0000	373.8274	0.1726	1.0000	0.1726	208.	23.0000	9.0600	0.0	0.0

Agreement Factors Based on Parameters Before Cycle 7

Sum (W*(0-C)**2) is 0.107E 02

SQRTF(Sum(W*(0-C)**2)/(NO-NV)) is 1.0368

Subroutine Test indicates that job is to be terminated for reason 2.

J.R. Cretney Base Cleavage M Chloro Run 5

Correlation Matrix:

1	1.0000	0.3676	0.0395
2	0.0	1.0000	0.9272
3	0.0	0.0	1.0000

(vi) Parameter values derived by program

	Parameter	Estimate	Error
1.	A_{Δ} (x1000)	519.8	1.55
2.	k_p (sec^{-1})	1.313×10^{-1}	1.335×10^{-4}
3.	A_f (x1000)	340.1	1.529

(vii) Explanation of output

The number of independent variables per observation is shown as 5, however only the 3 time variables are used, count time and background are redundant. All observations are given equal weight. KI(I) = 1 shows that the I^{th} parameter P(I) is to be varied.

Symbol	Meaning
Y(OBS), OBS, O	A_{obs}, observed absorbance (x1000)
Y(CALC),CALC,C	A_t, calculated absorbance (x1000)
ERROR	estimated standard errors of the parameter estimates
NO	number of observations
NV	number of parameters varied (=3)
W	weight (=1 since unit weights set by program)
SIG(0)	standard error in the observation (1.000 since $W = 1/\sigma^2$)
X(1)	observation time X(1) = X(2).X(3)
X(2)	observation position (cms)
X(3)	time/scan division ($sec.cm^{-1}$)
SUM(W*(0-C)**2)	$\Sigma W(0-C)^2 = \Sigma(0-C)^2$ sum of deviations square
SQRTF(SUM(W*(0-C)**2)/(NO-NV))	$\sqrt{\frac{\Sigma(0-C)^2}{NO-NV}}$ standard deviation of a point from the line.

APPENDIX B

The following illustrates the use of the ORGLS least squares program to examine linear free energy relationships. The example chosen is a Yukawa-Tsuno relationship involving the rate constants for the base cleavage of substituted phenyltrimethylsilanes

$$\log k_{rel} = \rho[\bar{\sigma} + r(\sigma^{+}-\sigma^{0})] + c$$

(i) Input Data

Approximate parameter values

1. $\rho = 7.00$
2. $r = 1.00$
3. $c = 0.10$

Table 30

Observed Rate Constants

Sub.	$\log k_{rel}$	$\bar{\sigma}$	$\sigma^{+}-\sigma^{0}$	Sub.	$\log k_{rel}$	$\bar{\sigma}$	$\sigma^{+}-\sigma^{0}$
m-NO_2	4.11	0.67	-0.03	m-Ph	0.58	0.07	0.06
p-NO_2	4.00	0.63	0.06	p-Ph	0.40	-0.03	-0.17
m-Br	2.86	0.39	0.02	m-OMe	0.34	0.07	-0.01
m-Cl	2.60	0.40	0.03	H	0.00	0.00	0.00
m-F	2.03	0.37	0.00	m-Me	-0.34	-0.08	0.00
p-Br	1.70	0.24	-0.11	p-Me	-0.58	-0.14	-0.16
p-Cl	1.54	0.23	-0.16	p-OMe	-0.63	-0.23	-0.62

(ii) Output

Run 219

Number of cycles in this job is 6.

Number of parameters to be varied is 3.

Number of independent variables per observation is 2.

Numerical derivatives unless parameter increment is zero.

Unit weights to be set by program.

Parameters to be read as input data.

Corrected parameters not to be saved for later use.

Number of parameters read is 3.

Number of observations read is 14.

Input data

I	P(I)	KI(I)	DP(I)
1	0.7000E 01	1	0.100E 00
2	0.1000E 01	1	0.100E 00
3	0.1000E 00	1	0.100E 00

Agreement Factors based on parameters before cycle 6.

SUM(W*(0-C)**2) is 0.473E 00

SQRTF(SUM(W*(0-C)**2)/(NO-NV)) is 0.2073

Run 219

Parameters after least squares cycle 6

	OLD	CHANGE	NEW	ERROR
1	6.0625	-0.0000	6.0625	0.2458
2	-0.1665	0.0000	-0.1665	0.0611
3	0.1291	0.0000	0.1291	0.0871

Estimated agreement factors based on parameters after cycle 6.

SUM(W*(0-C)**2) is 0.473E 00

SQRTF(SUM(W*(0-C)**2)/(NO-NV)) is 0.2073.

Run 219

Calculated Y based on parameters before cycle 7

Y(OBS)	Y(CALC)	OBS-CALC	SIG(0)	(0-C)/SIG(0)	X(1,I)	X(2,I)	X(3,I)
0.411E 01	0.422E 01	-0.111E 00	0.100E 01	-0.111E 00	0.670E 00	-0.300E-01	0.0
0.400E 01	0.389E 01	0.112E 00	0.100E 01	0.112E 00	0.630E 00	0.600E-01	0.0
0.286E 01	0.247E 01	0.387E 00	0.100E 01	0.387E 00	0.390E 00	0.200E-01	0.0
0.260E 01	0.252E 01	0.761E-01	0.100E 01	0.761E-01	0.400E 00	0.300E-01	0.0
0.203E 01	0.237E 01	-0.342E 00	0.100E 01	-0.342E 00	0.370E 00	0.0	0.0
0.170E 01	0.170E 01	0.484E-02	0.100E 01	0.484E-02	0.240E 00	-0.110E 00	0.0
0.154E 01	0.168E 01	-0.145E 00	0.100E 01	-0.145E 00	0.230E 00	-0.160E 00	0.0
0.580E 00	0.493E 00	0.870E-01	0.100E 01	0.870E-01	0.700E-01	0.600E-01	0.0
0.400E 00	0.119E 00	0.281E 00	0.100E 01	0.281E 00	-0.300E-01	-0.170E 00	0.0
0.340E 00	0.564E 00	-0.224E 00	0.100E 01	-0.224E 00	0.700E-01	-0.100E-01	0.0
0.0	0.129E 00	-0.129E 00	0.100E 01	-0.129E 00	0.0	0.0	0.0
-0.340E 00	-0.356E 00	0.159E-01	0.100E 01	0.159E-01	-0.800E-01	0.0	0.0
-0.580E 00	-0.558E 00	-0.219E-01	0.100E 01	-0.219E-01	-0.140E 00	-0.160E 00	0.0
-0.630E 00	-0.640E 00	0.952E-02	0.100E 01	0.952E-02	-0.230E 00	-0.620E 00	0.0

Agreement Factors based on parameters before cycle 7

SUM(W*(0-C)**2) is 0.473E 00

SQRTF(SUM(W*(0-C)**2)/(NO-NV)) is 0.2073

Run 219

Correlation matrix

1	1.0000	-0.4678	-0.7138
2	0.0	1.0000	0.5926
3	0.0	0.0	1.0000

(iii) Parameter values derived by program

	Parameter	Estimate	Error
1	ρ	6.0625	0.2458
2	r	-0.1665	0.0611
3	c	0.1291	0.0871

i.e. $\log k_{rel} = 6.06[\bar{\sigma} - 0.167(\sigma^{+}-\sigma^{0})] + 0.13$ (Fig. 10)

(iv) Explanation of output

The number of independent variables per observation is two, i.e. $\bar{\sigma}$ and $\sigma^{+}-\sigma^{0}$. All observations are given equal weight.

Symbol

Y(OBS), OBS, O	$\log k_{rel}$ (observed)
Y(CALC), CALC, C	$\log k_{rel}$ (calculated)
ERROR, NO, NV, W, SIG(0)	as in Appendix A
X(1,I)	first variable ($\bar{\sigma}$)
X(3,I)	second variable ($\sigma^{+}-\sigma^{0}$)
SUM(W*(O-C)**2) SQRTF(SUM*(O-C)**2)/(NO-NV))	as in Appendix A.

(v) Calculation of f

$$\text{R.M.S.} = \left(\frac{\sum_{i=1}^{N} (P^{i}_{obs})^{2}}{N} \right)^{\frac{1}{2}} = 2.047$$

$$\text{S.D.} = \left(\frac{\sum_{i=1}^{N} (P^{i}_{obs} - P^{i}_{calc})^{2}}{N} \right)^{\frac{1}{2}} = \left(\frac{0.473}{14}\right)^{\frac{1}{2}} = 0.184$$

$$f = \frac{0.184}{2.047} = 0.090.$$

APPENDIX C

Diagram Code for Linear Free Energy Correlations

1	m-NO_2	13	H
2	p-NO_2	14	m-Me
3	m-Br	15	p-Et
4	m-CF_3	16	p-Me
5	m-Cl	17	p-OMe
6	m-F	18	m-NMe_2
7	p-Br	19	p-NMe_2
8	p-Cl	20	p-SMe
9	p-F	21	m-NH_2
10	m-Ph	22	p-NH_2
11	p-Ph	23	m-CN
12	m-OMe	24	p-CN

As the $\bar{\sigma}$ scale is derived from a correlation using the σ^0 scale, the same error ($\mp$ 0.03) is used for both σ^0 and $\bar{\sigma}$ values. The horizontal components of points in the diagrams are based on this error. For the cleavage of aryltrimethylsilanes, the errors in log k_{rel} have also been calculated, but are not incorporated in the substituent points. For the other reactions included in the analysis, no errors were available.

REFERENCES

1. C. Eaborn, "Organosilicon Compounds", Butterworths 1960.
2. F.B. Deans, C. Eaborn, J. Chem. Soc. 2299 (1959).
3. C. Eaborn, J. Chem. Soc. 4858 (1956).
4. C. Eaborn, D.E. Webster, J. Chem. Soc. 4449 (1957).
5. H.C. Brown, Y. Okamoto, J.A.C.S. 80, 4979 (1958).
6. G.S. Hammond, J.A.C.S. 77, 334 (1955).
7. R.W. Bott, C. Eaborn, P.B. Greasley, J. Chem. Soc. 4804 (1964).
8. C.R. Hance, C.R. Hauser, J.A.C.S. 74, 1856 (1952).
9. H. Gilman, A.G. Brook, L.S. Miller, J.A.C.S. 75, 4531 (1953).
10. F.S. Kipping, N.W. Cusa, J. Chem. Soc. 1088 (1935).
11. I.P. Beletskaya, K.P. Butin, O.A. Reutov, Organomet. Rev. A7, 51 (1971).
12. D.G. Anderson, D.E. Webster, J. Chem. Soc. B 765 (1968).
13. F.H. Pinkerton, S.F. Thames, J. Heterocyclic Chem. 6, 433 (1969).
14. C. Eaborn, S.H. Parker, J. Chem. Soc. 126 (1955).
15. C. Eaborn, D.R.M. Walton, J. Organomet. Chem. 4, 217 (1965).
16. Khairat M. Ibne-Rasa, J. Chem. Ed. 44, 89 (1967).
17. C.G. Swain, C.B. Scott, J.A.C.S. 75, 141 (1953).
18. J.O. Edwards, J.A.C.S. 76, 1540 (1954).
19. J.O. Edwards, J.A.C.S. 78, 1819 (1956).
20. J.O. Edwards, R.G. Pearson, J.A.C.S. 84, 16 (1962).
21. Khairat M. Ibne-Rasa, J.O. Edwards, J.A.C.S. 84, 763 (1962).
22. G.D. Leahy, M. Liveris, J. Miller, A.J. Parker, Aust. J. Chem. 9, 382 (1956).

23. A.J. Parker, Chem. Rev. 69, 1 (1969).

24. K.H. Khoo, J. Chem. Soc. A, 2932 (1971).

25. R. Fuchs, K. Mahendran, J. Org. Chem. 36, 730 (1971).

26. R.K. Wolford, J. Phys. Chem. 68, 3392 (1964).

27. G. Satzinger, Tetrahedron 3739 (1971).

28. C.J. Attridge, Organomet. Rev. A5, 323 (1970).

29. K.S. Pitzer, J.A.C.S. 70, 2140 (1948).

30. R.S. Mulliken, J.A.C.S. 72, 4493 (1950).

31. A.A. Levin, Ya.K. Syrkin, M.E. Dyatkina, Zhim. Struct. Khim. 8, 317 (1967).

32. C.P. Craig, A. Macoll, R.S. Nyholm, L.E. Orgel, L.E. Sutton, J. Chem. Soc. 332 (1954).

33. A.B. Burg, E.S. Kuljian, J.A.C.S. 72, 3103 (1950).

34. R. West, R.H. Baney, J.A.C.S. 81, 6145 (1959).

35. R.H. Baney, K.J. Lake, R. West, L.S. Whatley, Chem. & Ind. 1129 (1959).

36. H. Vahrenkamp, H. Nöth, J. Organomet. Chem. 12, 281 (1968).

37. H. Soffer, T. de Vries, J.A.C.S. 73, 5818 (1951).

38. H. Freiser, M.V. Eagle, J. Speier, J.A.C.S. 75, 2821 (1953).

39. H.H. Huang, K.M. Hui, J. Organomet. Chem. 2, 288 (1964).

40. J.A. Bedford, J.R. Bolton, A. Carrington, R.H. Prince, Trans. Far. Soc. 59, 53 (1963).

41. M.D. Curtis, A.L. Allred, J.A.C.S. 87, 2554 (1965).

42. L. Goodman, A.H. Konstam, L.H. Sommer, J.A.C.S. 87, 1012 (1965).

43. J.A.A. Keteelar, Z. Kristallog. 92, 155 (1935).

44. W. Dilthey, Ber. Dtsh. Chem. Ges. 36, 932 (1903).

45. D.I. Cook, R. Fields, M. Green, R.N. Hazeldine, B.R. Iles, A. Jones, M.H. Newlands, J. Chem. Soc. A 887 (1966).

46. C.A. Coulson, Nature 221, 1106 (1969).

47. R. West, J.A.C.S. 80, 3246 (1958).

48. R. West, J. Org. Chem. 23, 1552 (1958).

49. J.W. Linnett, C.E. Mellish, Trans. Far. Soc. 50, 665 (1954).

50. H.A. Bent, Organic Sulphur Compounds Vol. 2 (ed. Kharash & Meyers) 1966.

51. A.A. Humffray, J.J. Ryan, J. Chem. Soc. B 1138 (1969).

52. S. Dyankov, D. Shopov, Chem. Abst. 65, 12070 (1956).

53. L.H. Sommer, O.F. Bennett, P.G. Campbell, D.R. Weyenberg, J.A.C.S. 79, 3295 (1957).

54. L.H. Sommer, O.F. Bennett, J.A.C.S. 81, 251 (1959).

55. D.G. Anderson, D.E. Webster, J. Chem. Soc. B 878 (1968).

56. L.H. Sommer, C.L. Frye, G.A. Parker, J.A.C.S. 86, 3276 (1964).

57. M.I.T. Seminars, 193, 1965 (I).

58. R. Baker, R.W. Bott, C. Eaborn, P.W. Jones, J. Organomet. Chem. 1, 37 (1963).

59. L.H. Sommer, P.G. Rodewald, J.A.C.S. 85, 3898 (1963).

60. C.G. Swain, R.M. Esteve, R.H. Jones, J.A.C.S. 71, 965 (1949).

61. C. Eaborn, H. Hornfeld, D.R.M. Walton, J. Chem. Soc. B, 1036 (1967).

62. R. Alexander, C. Eaborn, T.G. Traylor, J. Organomet. Chem. 21, P65 (1970).

63. R.W. Bott, C. Eaborn, T.W. Swaddle, J. Chem. Soc. 2342 (1963).

64. S. Ehrenson, R.T.C. Brownlee, R.W. Taft (in press).

65. R.W. Taft, J. Phys. Chem. 64, 1805 (1960).

66. A.R. Bassindale, C. Eaborn, R. Taylor, A.R. Thompson, D.R.M. Walton, J.R. Cretney, G.J. Wright, J. Chem. Soc. B 1155 (1971).

67. A. Streitweiser, R.G. Lawler, J.A.C.S. 87, 5388 (1965).

68. Private Communication, C. Eaborn.

69. Y. Yukawa, Y. Tsuno, Bull. Soc. Chim. Jap. 32, 971 (1959). Y. Yukawa, Y. Tsuno, M. Sawada, Bull. Soc. Chim. Jap. 39, 2274 (1966).

70. W.J. Galloway, Ph.D. Thesis, University of Canterbury (1965).

71. H.C. Brown, D.H. McDaniel, J.A.C.S. 77, 3752 (1955).

72. A.R. Katritsky, P. Simmons, J. Chem. Soc. 1511 (1960).

73. C.D. Ritchie, E.S. Lewis, J.A.C.S. 84, 591 (1962).

74. M.L. Crossley, R.A. Kienle, C.H. Benbrook, J.A.C.S. 62, 1400 (1940).

75. J.D. Dickson, C. Eaborn, J. Chem. Soc. 3036 (1959).

76. E.S. Lewis, L.D. Harting, B.M. McKay, J.A.C.S. 91, 419 (1969).

77. G. Marino, Advances in Heterocyclic Chem. 13, 235 (1971).

78. C. Eaborn, J.A. Sperry, J. Chem. Soc. 4921 (1961).

79. F.B. Deans, C. Eaborn, J. Chem. Soc. 2303 (1959).

80. Yu.I. Shapiro, L.I. Belen'kii, I.A. Romanskii, F.M. Stoyanovich, Ya.L. Goldforb, A.I. Shatenstein, J. Gen. Chem. USSR 38, 1938 (1968).

81. J.R. Jones, Prog. Phys. Org. Chem. 9, 241 (1972).

82. D. Dolman, R. Stewart, Can. J. Chem. 45, 911 (1967).

83. J.R. Jones, R. Stewart, J.A.C.S. 89, 5069 (1967).

84. J.R. Jones, Chem. Brit., 336 (1971).

85. B.G. Cox, P.T. McTigue, Aust. J. Chem. 20, 1815 (1967).

86. A.G. Sharkey, R.A. Friedel, S.H. Langer, Analyt. Chem. 29, 770 (1957).

87. J.R. Cretney, B.Sc.(Hons.) Report (1968).

88. A.E. Newkirk, J.A.C.S. 68, 2736 (1946).

89. W.T. Grubb, J.A.C.S. 76, 3408 (1954).

90. E.J. Corey, M. Chaykovsky, J.A.C.S. 87, 1345 (1965).

91. C. Agami, M. Caillot, Bull. Soc. Chim. Fr. 1990 (1969).

92. J.J. Delpuech, Tet. Letters 2111 (1965).

93. W.R. Busing, H.A. Levy, "O.R.G.L.S., a General Fortran Least Squares Program", Oak Ridge National Laboratory U.S.A.E.C. 1962.

94. E.A. Guggenheim, Phil. Mag. 2, 538 (1926).

95. H.A. Clark, A.F. Gordon, C.W. Young, M.J. Hunter, J.A.C.S. 73, 3798 (1951).

96. F.B. Deans, C. Eaborn, J. Chem. Soc. 498 (1957).

97. L.W. Frost, J.A.C.S. 78, 3855 (1956).

98. R.A. Benkeser, R.A. Hickner, D.I. Hoke, O.H. Thomas, J.A.C.S. 80, 5289 (1958).

99. C.A. Burkhard, J.A.C.S. 68, 2103 (1946).

100. J.D. Roberts, E.A. McElhill, R. Armstrong, J.A.C.S. 71, 2923 (1949).

101. O. Diels, F. Bunzl, Ber. 38, 1486 (1905).

102. R.A. Benkeser, H.R. Krysiak, J.A.C.S. 75, 4528 (1953).

103. C. Eaborn, J. Chem. Soc. 3148 (1953).

104. R.G. Severson, R.J. Rossoup, J.A.C.S. 76, 4552 (1954).

105. H. Gilman, I. Banner, J.A.C.S. 62, 344 (1940).

106. A. Mendel, J. Organomet. Chem. 6, 97 (1966).

107. H. Gilman, N.W. Melvin, J.J. Goodman, J.A.C.S. 76, 3219 (1954).

108. Organic Reactions Vol. VI.

109. R.A. Benkeser, R.B. Currie, J.A.C.S. 70, 1780 (1948).

110. Organic Synthesis, Vol. 44, 9.